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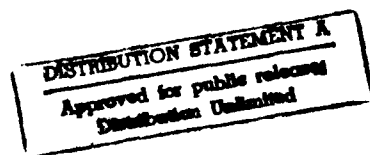
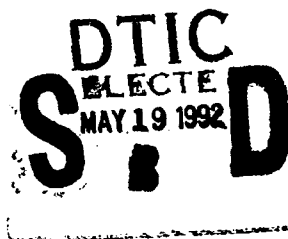


RAD 6744-MS 02

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THIRD INTERNATIONAL WORKSHOP
ON NON-CRYSTALLINE SOLIDS

PROGRAMME
AND
ABSTRACTS



Matalascañas (Costa de la Luz)
Spain
November 5-8, 1991

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PERKIN ELMER HISPANIA

PROGRAMME

Monday, 4th

Afternoon/Evening

Arrival at the airport (or railway station) Sevilla.

Transport by bus from Sevilla to
Matalascañas (Huelva).

Accommodation in the "Gran Hotel del Coto"
in Matalascañas.

Tuesday, 5th

Morning

- | | |
|---------------|---|
| 08.30 - 09.30 | Registration |
| 09.30 - 10.00 | Opening session |
| 10.00 - 11.00 | Invited lecture I-1 R.W. Cahn: "Mechanical Amorphization of Ordered Intermetallic Phases". |
| 11.00 - 11.30 | Coffee break |
| 11.30 - 12.30 | Invited lecture I-2 J.M. Dubois: "Non Crystalline Aluminium rich Alloys: Fundamentals and Applications". |
| 12.30 - 13.30 | Invited lecture I-3 F.J. Baltá: "Influence of the Crystallization on the Mechanical Properties of Poly (ethylene terephthalate)" |

Afternoon

- | | |
|---------------|--|
| 16.00 - 17.00 | Invited lecture I-4 G. Herzer: "Microstructure and Magnetism in Nanocrystalline Ferromagnets" |
| 17.00 - 17.30 | Coffee break |
| 17.30 - 18.30 | Oral session O1 |
| 18.30 - 20.00 | Poster session P1 |
| 20.30 | Cocktail |

Wednesday, 6th

Morning

09.00 Excursion to Sevilla.

Evening

Return to Matalascañas

Thursday, 7th

Morning

09.00 - 10.00 Invited lecture I-5
H. Matyja: "Nanocrystalline Alloys obtained by Crystallization of
Metallic Glasses"

10.00 - 11.00 Invited lecture I-6
A. van den Beukel: "Structural Relaxation in Metallic Glasses"

11.00 - 11.30 Coffee break

11.30 - 12.00 Invited lecture I-7
J. Jackle: "Cooperativity of Molecular Motion in Liquids near the
Glass Transition"

12.30 - 13.30 Oral session O2

Afternoon

16.00 - 17.00 Invited lecture I-8
H.T. Savage: "Magnetoelastic Interactions in Amorphous
Ferromagnets - Theory and Applications"

17.00 - 17.30 Coffee break

17.30 - 18.30 Oral session O3

18.30 - 20.00 Poster session P2

21.30 Conference dinner

Friday, 8th

Morning

- | | |
|---------------|---|
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| 10.00 - 11.00 | Invited lecture I-10 H.G. Zachmann: "Studies of Structure and Glass Transition in Liquid Crystalline Polymers by Means of Synchrotron Radiation and Complementary Methods" |
| 11.00 - 11.30 | Coffee break |
| 11.30 - 12.30 | Invited lecture I-11 G.R. Strobl: "On the Nature of the Partially Crystalline State of Polymeric Solids" |
| 12.30 - 13.30 | Oral session O4 |

Afternoon

- | | |
|---------------|--|
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| 17.30 - 18.30 | Oral session O5 |
| 18.30 - 20.00 | Poster session P3 |
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ABSTRACTS

Mechanical Amorphization of Ordered Intermetallic Phases

R.W. CAHN
(University of Cambridge)

The discovery that certain ordered intermetallic phases can be amorphized by intense mechanical deformation was reported in 1983, and since then, the technique has been applied to a great variety of alloys. The favourite technique is ball-milling of powders, followed by intense rolling or wire-drawing of finely divided strips or wires of elementary metals in contact; i.e., the starting material may be either a readymade intermetallic phase or else the constituent elements.

Various generalizations have been proposed concerning the factors that determine whether a particular intermetallic phase can be mechanically amorphized. A particular topic of current discussion is whether the essential precondition is the destruction of long-range order or whether, alternatively, the important thing is to expand the lattice (which is an incidental byproduct of disordering). In this connection, the theoretical parallels between (solid-state) amorphization and melting have received special attention. These issues are surveyed in the paper.

NON-CRYSTALLINE ALUMINIUM RICH ALLOYS :
FUNDAMENTALS AND APPLICATIONS

Jean-Marie Dubois

Laboratoire de Science et Génie des Matériaux Métalliques
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F- 54042 NANCY

Non-crystalline aluminium alloys reached the status of fascinating materials from the fundamental point of view during the past decade. The field was opened in 1982 when the author, in collaboration with G. Le Caer, produced amorphous ribbons of aluminium rich alloys in sizeable amounts (1). Other alloys of interest were discovered latter on in Al-transition metal-rare earth systems (2,3). The glass forming conditions for those alloys will be reviewed and some properties, of potential technological significance, will be evocated.

A dramatic change occurred in crystallography after the first report by Shechtman et al. (4) on five-fold symmetry in Al-transition metal alloys. Many structural characteristics as well as physical properties, both fundamental and applied, relate those so-called quasicrystalline compounds to the glassy state. This data will be discussed. Finally a brief attempt will be made to frame a few application domains of these alloys that may bring non-crystalline aluminium alloys to an even more interesting stand point during the present decade.

- 1- J.M. DUBOIS, G. LE CAER, Compt. Rend. As. Sc., Paris 301, 73, (1985)
- 2- A. INOUE, K. OHTERA, A.P.TSAI, T. MASUMOTO, Jap. J. Appl. Phys 27, L280, (1988)
- 3- Y. HE, S.J. POON, G.S. SHIFLET, Science 241, 1640, (1988)
- 4- D. SHECHTMAN, I. BLECH, D. GRATIAS, J.W. CAHN, Phys. Rev. Lett. 53 1951, (1984)

INFLUENCE OF THE CRYSTALLIZATION ON THE MECHANICAL
PROPERTIES OF POLY(ETHYLENE TEREPHTHALATE)

F.J. Baltá Calleja

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The use of microhardness (H) is well established as a technique which can detect changes in the microstructure of polymers. Microhardness is, furthermore, directly correlated with the yield stress (Tabor's relation) and to the elastic modulus of the material. The aim of the present study is to examine the hardness-microstructure correlation in case of low crystallinity systems having a T_g -value well above room temperature. For this purpose poly(ethylene terephthalate) (PET) samples prepared in the glassy state were investigated. The kinetics of crystallization from the glassy state was studied in real time by measuring the microhardness for different crystallization temperatures. Results are discussed in terms of the Avrami equation. Values of the Avrami exponent, n , of about 3 are observed for all samples without nucleating agent (homogeneous nucleation) and with nucleating agent. For the latter samples two crystallization ranges are observed: A first range which corresponds to a fast crystallization from nucleating agent particles and a second range which is associated to a slow self-crystallization mode. New precrystallization phenomena evidenced by the presence of a small maximum in H as a function of annealing temperature are observed at temperatures higher than T_g for the physically aged samples. The kinetics of this precrystallization transition has also been examined. It is further shown that the presence of nucleating agent induces a hardening at room temperature which is similar to the effect produced by the physical aging of the samples below T_g . Finally, it is found that aging reduces the rate of creep of the material under the indenter.

MICROSTRUCTURE AND MAGNETISM IN NANOCRYSTALLINE FERROMAGNETS

Giselher Herzer
Vacuumschmelze GmbH, D-6450 Hanau, Germany

Nanocrystalline materials offer a new opportunity of tailoring good soft magnetic properties. The most prominent example is devitrified glassy FeCuNbSiB which reveals a homogeneous ultrafine grain structure of bcc-FeSi with grain sizes of typically 10-20nm and random texture.

The key for understanding the soft magnetic properties of nanocrystalline materials is to recognize that the average grain size is smaller than the ferromagnetic exchange length (about 40nm for bcc-FeSi). Thus the local magneto-crystalline anisotropy is randomly averaged out so that there is only a small anisotropy net-effect on the magnetization process.

An additional highlight of nanocrystalline Fe-base alloys is their low or vanishing saturation magnetostriction, λ_s , which can be understood from the structural phases present.

Both the suppressed magneto-crystalline anisotropy and the low magnetostriction provide the basis for the superior soft magnetic properties comparable to those of permalloys or near zero-magnetostrictive Co-base amorphous alloys.

NANOCRYSTALLINE ALLOYS OBTAINED BY CRYSTALLIZATION OF METALLIC GLASSES

H. Matyja and T. Kulik

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Poland

Nanocrystalline materials can be created by crystallization of metallic glasses using special heat treatment eg. flash annealing[1,2] or by conventional annealing of glasses with appropriate composition[3]. This ultrafine structure can result in novel and/or enhanced properties.

The aim of this paper is to study the role of composition and heat treatment of amorphous alloys on their structure.

Amorphous Fe- and Co-based ribbons were prepared in air by the single-roller chill block melt spinning method. Flash annealing was performed in liquid nitrogen. An electric current of 20A (resulting in a current density of 280 MA m^{-2}) and pulse length in the range 30 to 40 ms was applied. Crystallization products were studied using x-ray diffractometry and transmission electron microscopy (TEM).

It was found, that nanocrystalline structure can be created by conventional furnace annealing only in alloys with special composition, eg. in Fe-Si-B alloys containing at least two alloying elements: Cu and Nb or Cu and Ta. Flash annealing results in substantial grain refinement of crystallization products and makes possible creation of ultrafine structure with grain diameter less than 30 nm in all the glasses studied in this work.

References

1. H. Matyja and A. Zaluska, Phil. Mag. B61(1990)701
2. T. Kulik, D. Bucka and H. Matyja, to be published
3. Y. Yoshizawa, K. Yamauchi and S. Oguma, European Patent Application 0 271 657 (22.06.1988)

Structural relaxation in metallic glasses

A. van den Beukel

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Abstract

Prior to crystallisation, in metallic glasses a change in many physical properties has been observed, which must be due to atomic rearrangements within the amorphous state. This phenomenon is called "structural relaxation". In this paper the experimental data is analysed in terms of a model of the underlying physical processes.

Two types of processes can be distinguished: 1. Those which are reversible with temperature and ascribed to chemical short range ordering (CRSO). 2. Irreversible processes which are due to the annealing out of excess free volume (TRSO). CRSO comes first and consists of a series of processes with a wide spectrum of activation energies. It is followed by TRSO, a process with well defined kinetics and a single value of the activation energy. There are also strong indications that in the "CRSO range" of as-quenched specimens irreversible processes (as yet unidentified) play a part.

In the description of TSRO it is important to distinguish between two types of physical properties: 1. Properties which are related to the average free volume, like density, electrical resistivity and elastic constants. 2. Properties which are connected with atomic mobility and therefore "defect controlled", like viscosity and diffusivity. The description of the behaviour of these properties makes it necessary to introduce two types of defects: Flow defects (concentration c_f) for the description of viscosity and diffusion defects (concentration c_d) for the description of diffusivity. A consistent description of the experimental data is obtained when it is assumed that $c_d \sim c_f^{1/2}$. The physical basis of this relation is as yet not understood.

Finally it is shown that the glass transition in metallic glasses can be quantitatively understood when it is described as a free volume related kinetic phenomenon.

Cooperativity of Molecular Motion in Liquids near the Glass Transition

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The dynamics of molecular motion in undercooled liquids near the glass transition has been commonly interpreted in terms of a "cooperative rearrangement" of molecules (Adam and Gibbs 1965) or, more recently, of a "hierarchically constrained" sequence of processes (Palmer, Stein, Abrahams and Anderson 1984). In this lecture a family of lattice-gas and kinetic Ising models with kinetic constraints are presented, which model the complicated geometrical and energetic conditions of molecular relaxation in glass-forming liquids in a relatively simple way. The study of the models is of interest

- 1) from an experimental point of view, since they define a "characteristic length of cooperativity" and indicate the possible existence of size effects in the relaxational or transport properties of glass-forming liquids in confined geometries,
- 2) from a theoretical point of view, since they help to clarify
 - the theoretical basis of empirical formulae such as the Kohlrausch-Williams-Watts formula
 - the conditions for the occurrence of different types of blocking transitions ("dynamical phase transitions")
 - the validity of various theoretical approximation methods.

MAGNETOELASTIC INTERACTIONS IN AMORPHOUS FERROMAGNETS-THEORY AND APPLICATIONS

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Amorphous ferromagnetic alloys offer an option in material engineering not available in crystalline materials. The main reason for the usefulness of these materials is that the linear magnetostriction and magnetic anisotropy can be controlled by composition and heat treatment. Values of magnetic anisotropy can be as low as 30J/m^3 in Fe-B-Si alloys. These alloys have a magnetostriction about the same as Ni ($30\text{-}40 \times 10^{-6}$) but with a magnetic anisotropy orders of magnitude lower than Ni. This is extremely important for stress sensing. In some applications such as magnetometers zero magnetostriction magnetic material is desired. This can be achieved by alloying with Co. Values of magnetostriction can be as low as 10^{-8} . The result of this is either significant commercial efforts or actual marketing of devices such as torque sensors, strain gages, accelerometers, price tags, security devices, transformers, coding devices, counters and magnetometers.

The material has been available in ribbon form for many years. The magnetization process is well understood in this geometry. We will present a theory of the ΔE effect (the change in Young's modulus with magnetic field) which is the basis for the description of the stress sensitivity. This theory, which fully describes the nonlinear stress-strain relationship in the material, shows the reasons for the high figures of merit in stress sensing, shows the conditions for paramagnetic amplification, and shows the basis for a fundamental nonlinear dynamics experiment. This intrinsically nonlinear buckling ribbon experiment has shown for the first time, among other things, the control of chaos. In this experiment the system is first put into chaotic motion and then is taken out of its chaotic motion by stabilizing one of the unstable periodic orbits that exist in a chaotic system.

We will also present new work in magnetoelastic amorphous wires. This circular geometry is more robust than the ribbon geometry and has advantages in some applications. Here the magnetization process is not well understood when the wires are well annealed with a transverse magnetic field. Large Barkhausen jumps can characterize the magnetization process in annealed and unannealed positive magnetostriction wire. A survey of what is known of the magnetization process will be presented. Torque sensor work will be delineated. The start of a general theory for magnetoelastic effects in cylindrical geometries will be shown.

**UNCONVENTIONAL METHODS FOR OBTAINING GLASSES
AND
AMORPHOUS MATERIALS**

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To obtain glasses or amorphous solids it is necessary to retain at ambient temperatures the disordered state of a liquid or gas or, alternatively, to destroy the crystalline arrangement. It is also possible to produce the disordered structure by means of suitable chemical reactions in liquid phase which may or may not be assisted by external fields derived from chemical, mechanical or electrical potentials.

The traditional way of obtaining glass is by quenching a supercooled melt which process is strongly dependent on the speed of cooling. Various technical devices were imagined using hyperquench which permitted a substantial extension of vitrification domains and led to new types of glasses.

Vapour quenching in its numerous variants (thermal evaporation, sputtering, glow discharge decomposition and CVD) can be used to produce amorphous materials mainly in thin layer form.

Crystalline solid disordering may be achieved by irradiation, mechanical shock, attrition or interdiffusion processes.

Finally, reactions in solution, e.g. the "sol-gel" process, use soft chemistry to build up disordered lattices which may be converted into compact glass structures.

Respective advantages and limitation of these various methods are examined and their eventual influence on the resulting final products discussed.

Studies of Structure and Glass Transition in Liquid Crystalline
Polymers by Means of Synchrotron Radiation and Complementary
Methods

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Binary and ternary copolyesters of poly(ethylene terephthalate), poly(ethylene naphthalene-2,6-dicarboxylate), and p-hydroxybenzoic acid have been synthesized having a wide range of different compositions. The influence of the composition on the crystallization behaviour and on the ability to form liquid crystalline states was investigated. The molecular order in these states, the glass transition temperature, the phase transition temperatures, and the rate of crystallization were determined by means of DSC, dynamic mechanical analysis, microscopy, and X-ray scattering employing synchrotron radiation.

It was shown that liquid crystalline states are formed if the PHB content exceeds 35%. However, the material is only partially liquid crystalline as long as the PHB content is less than about 50%. In some materials both the complete isotropic and the complete liquid crystalline state can be frozen in, depending on the thermal pretreatment. The glass transition temperature of the liquid crystalline phase is about 20°C lower than that of the isotropic state. The PET and PEN crystallizes if the amount of these units is higher than 50%. PHB cannot form the usual crystal structure even if present up to 90%. The kinetics of phase transitions show an interesting dependence on the composition and structure of the different copolymers.

ON THE NATURE OF THE PARTIALLY CRYSTALLINE STATE OF
POLYMERIC SOLIDS

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The structure of partially crystalline polymeric solids is controlled by kinetic factors rather than by equilibrium thermodynamics. Cooling from the melt usually results in the formation of a lamellar structure built of stacked crystalline and amorphous layers. The thickness of the crystallites and the crystallization rate show characteristic temperature dependencies, which can be related to the melting point depression of microscopic crystals and a specific sequence length dependence of the attachment rates. In most cases crystallization starts at nuclei and proceeds by the growth of spherulites. In the special case of crystallization in cold-drawn fibers an alternative continuous crystallization mode is observed, which is reminiscent of the process of spinodal decomposition. After completion of the kinetical transformation at the chosen temperature crystallization continuous further upon cooling. Two processes contribute to this further enhancement of the crystallinity: a continuous shift of the crystalline-amorphous interface reducing the thickness of the amorphous layers, and the formation of additional thin crystallites, which become inserted between the already existing ones. Both processes are largely reversible with temperature. Evidence for the different processes and a characterization of the partially crystalline state is provided by temperature dependent experiments, using

- small angle X-ray scattering (determination of layer structure parameters)
- Raman spectroscopy (chain conformations in crystallites, the melt-like phase and transition regions)
- quasielastic neutron scattering (study of the confined segmental motion in the amorphous layers)

"Ionic conduction in glass"

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Ion transport in glasses and amorphous materials finds many applications, most notably in sensors, in advanced battery systems, in electrochromic devices, and in changing the optical and mechanical properties of glass surfaces through cation-exchange processes. Nevertheless, an agreed theoretical treatment has been missing, and topics such as the "mixed alkali effect" continue to arouse lively controversy.

To some extent these problems reflect our ignorance of glass structure and how it influences the dynamics of ion migration. This paper will describe a simple conceptual framework which seems able to treat the whole range of ion transport processes in terms of both short-range ($<5\text{\AA}$) and medium-range structure ($10\text{-}15\text{\AA}$), and the corresponding "memory effects" which it is suggested are characteristic of the vitreous state.

NANOCRYSTALLINE MATERIALS BY CRYSTALLIZATION OF ZR-BASED METALLIC GLASSES

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Crystallization of metallic glasses proceeds by nucleation and growth processes. Thus controlling these processes enables tailor-made microstructures, e.g. nanocrystalline materials.

In metal-metalloid glasses below the glass transition these processes are controlled by diffusion and nucleation is heterogeneously, above the glass transition crystallization is controlled by viscous flow and nucleation occurs by a transient type homogeneous reaction. Microstructures with the smallest grain size can be formed by polymorphous crystallization only at temperatures above the glass transition temperature, but still far below the "nose" in the TTT-diagram. The smallest grain size in (Fe,Ni)₇₅B₂₅-glasses observed was about 0.1 μm . Further decrease in the grain size in metal-metalloid glasses can be achieved by primary crystallization with time-dependent growth rates.

In zirconium-based intertransition metal glasses with 67 at.% Zr crystallization behaviour probably do not exhibit any change at the glass transition. At temperatures below the glass transition nucleation of the tetragonal equilibrium phase has been observed to be proceed by a transient type homogeneous reaction. Above the glass transition temperature, however, instead of this reaction the very fast crystallization of a metastable fcc-phase (e.g., CoZr₂: $a = 12.2 \text{ \AA}$) was observed thus leading to a nanocrystalline microstructure. In Co₃₃Zr₆₇ this metastable compound transforms during further annealing into another metastable phase with hexagonal structure ($a = 8.76 \text{ \AA}$; $c = 19.5 \text{ \AA}$). The equilibrium phase can be achieved only after annealing times comparable with those extrapolated from the crystallization process below the glass transition temperature.

In binary as well as ternary (Cu,Ni,Co,Fe)₃₃Zr₆₇ glasses kinetics of these crystallization reactions were studied in detail by quantitative metallography as well as by time-resolved x-ray diffraction using synchrotron radiation, thus leading to time-temperature-crystallization diagrams. The stability of binary TMZr₂-glasses has been found to increase in the sequence: Ni \rightarrow Co \rightarrow Fe and is closely related to the filling of the d-band.

It is not clear whether the nanocrystalline metastable fcc-phase is a precursor to the formation of the equilibrium phase at all temperatures and even below the glass transition temperature. The observed results will be discussed with regard to the glass transition in the different metallic glasses.

MICROSTRUCTURAL STUDIES OF NANOCRYSTALLINE AND AMORPHOUS PHASE FORMATION BY MILLING TECHNIQUES

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The formation of amorphous phases can occur during ball-milling of elemental powders because the highly energetic disordered states of the systems created by milling hinder the existence of the corresponding ordered crystallographic structures. Other metastable disordered phases can form instead or as precursors to the amorphous ones. Dealing with such structures appears unavoidable when the formation of nanocrystalline intermetallic compounds is desired.

The aim of the present study has been to characterise the different phases obtained prior to or instead of intermetallic compounds during the milling process. The evolution of the milled microstructures has been followed by transmission and scanning electron microscopy together with x-ray diffraction of the powders for different alloy systems. Although the formation of the amorphous phases appears to occur when using x-ray diffraction techniques, detailed TEM examinations of the powders has revealed the presence of nanocrystals embedded in an amorphous matrix in most cases. The appearance and disappearance of metastable phases has been shown to occur in some cases and total amorphisation has been shown to be a rare exception.

CRYSTALLIZATION KINETICS IN NANOCRYSTALLINE MATERIALS

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During the last decades metallic glasses have been intensely studied for their physical as well as technically applicable properties, but it is known that their excellent magnetic properties are irreparably lost upon crystallization. The discovery of a new ferromagnetic iron-based class of metallic glasses brings about amorphous materials which exhibit outstanding magnetic properties after partial crystallization [1]. An example of such new materials is Fe_{73.5}Cu₁Nb₃Si_{13.5}B₉. The samples were cast initially as amorphous ribbons, and by subsequent annealing above the crystallization temperature a homogeneous ultrafine grain structure of α -Fe(Si) with a typical grain diameter of 10-20 nm and random texture was created within the amorphous matrix.

The aim of our work is to report detailed information on the crystallization behaviour of this primary crystallizing metallic glass. The crystallization study was performed by differential scanning calorimetry (DSC), X-ray diffraction and transmission electron microscopy (TEM). The calorimetric results show that there are several stages of crystallization. Transmission electron microscopy of the specimens after controlled heat treatment shows that the primary crystallization of α -(Fe,Si) in the amorphous matrix occurs in the first stage of crystallization. X-ray diffraction experiments confirm these results. From the crystallization kinetics results the low part of the T-T-T and T-HR-T curves of the crystallization processes are deduced [3].

1. Y. Yoshizawa, S. Oguma and K. Yamauchi, J. Appl. Phys. 64 (1988) 6044.
2. G. Herzer, Mater. Sci. Eng., A133 (1991) 1.
3. S. Suriñach, M.D. Baró, J.A. Diego, N. Clavaguera and M.T. Clavaguera-Mora, Acta Met. Mater., (1991) in press.

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BISTABLE BEHAVIOUR IN STRESS-ANNEALED NON-MAGNETOSTRICTIVE AMORPHOUS WIRE

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Magnetic properties of high-magnetostrictive amorphous wires have been extensively studied during the last few years. Mainly, it is due to the occurrence of large Barkhausen jump at low field that makes them suitable for technological applications such as sensor elements. This property is attributable to the anisotropy caused by the interaction between magnetostriction and internal stresses quenched-in during solidification. So, in as-cast state, non-magnetostrictive amorphous wires do not present bistable behaviour.

However, as in the case of amorphous ribbons, it is possible to induce macroscopic magnetic anisotropies by thermal treatments under the action of magnetic field or/and applied stress. In the present work, a nearly non-magnetostrictive ($\lambda_s \approx 4 \cdot 10^{-7}$) Co-rich amorphous wire has been annealed under an applied tensile stress by means of flowing a current through the wire. Isochronal treatments (6 min) were performed for a series of different applied stresses. In this way, we have found that it is possible to get bistable behaviour in non-magnetostrictive amorphous wire. Induced anisotropies and changes of magnetostriction are studied as a function of applied stress during annealing. Moreover, temperature dependence of DC hysteresis loops from 10K to 300K is also reported. The appearance of bistability and the temperature dependence of the corresponding switching field (field at which a large Barkhausen jump takes place) are interpreted as a consequence of the variations in anisotropy taking place with annealing and temperature respectively.

GLASS TRANSITION AND PHYSICAL AGING IN AMORPHOUS
POLY(ETHYLENE TEREPHTHALATE).

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Glassy polymers are known to undergo changes with time in their physical and mechanical properties when annealed at a temperature close to but below their glass transition temperature. The best documented effect under these conditions is the volume recovery exhibiting both non linear effect and thermal history effects but this phenomenon can be studied by probing not only thermodynamic properties but also all properties depending on molecular mobility.

In this study, comparisons are made between experimental results obtained by DSC and Dynamic Mechanical Spectroscopy experiments and simulations. The latter are obtained from a physical model assuming diffusion and annihilation of "quasi point defects". This model takes also into account a distribution of the defect mobility, and then is able to describe the structural relaxation and to reproduce, with the same set of parameters, both DSC and DMS experiments.

Evolutions of the distribution of defect mobility during physical aging treatments and DSC or DMS experiments leads to physical understanding of the different aspects of the observed phenomena : more especially shape, amplitude and displacement in temperature of the endothermal peak observed in DSC experiments after various aging treatments, existence of a sub-T_g peak after physical agings carried out at low temperature.

**THE STRUCTURE AND OPTICAL PROPERTIES
OF PHOSPHATE GLASSES WITH IRON IONS**

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Phosphate glasses were melted under appropriate conditions with iron ions /about 1 wt %/ in order to obtain glasses with Fe^{2+} and Fe^{3+} ions.

The structure of the obtained glasses was determined using Raman spectra. Some physico-chemical properties, especially light transmittance were also established.

The analysis of Raman spectra of the examined glasses has revealed the presence of metaphosphate and ortophosphate groups in the glass. Phosphate glasses with Fe^{2+} ions exhibit maximum light transmittance in the range 400-700 nm, and an almost complete absorption in the range 900-1100 nm, contrary to glass containing Fe^{3+} . Retaining the Fe^{2+} ions in the glass is in practice possible only in the phosphate glass. This property of the glass qualifies it to be used for optical filters for neodymium lasers.

EXAFS AND XANES STUDY OF SILICA-TITANIA GELS AND GLASSES

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The first and second neighbours arrangement around Ti atoms were studied in gels and glasses of the $x \text{ TiO}_2 - (1-x) \text{ SiO}_2$ system with $x = 5$ and $x = 10$ from X-ray absorption spectroscopy. Because of the Ti low concentration, fluorescence detection was used. EXAFS and XANES spectra were performed at room temperature at the K-edge of Ti, with radiation emitted by the L.U.R.E. (Orsay, France) DCI storage ring at the EXAFS-III beam station.

From the comparison of XANES spectra with those of SrTiO_3 and rutile TiO_2 , an octahedral environment of Ti can be inferred, where the octahedra are distorted as in the case of TiO_2 .

EXAFS spectra give information about the coordination spheres. In the cases under study, first and second peaks of the Fourier Transform of EXAFS signal were suitable for discussion. The first one gives an approximate distance of $1.95 \pm 0.05 \text{ \AA}$ for the Ti-O bond length which abides by our former discussion from x-ray diffraction analysis [1]. Some differences are observed in the second peak, which are related to the Ti-O-Si and Ti-O-Ti distances, regarding to the method of preparation and heat-treatments.

- [1] J.M. Ruiz-Rube, M. Ramírez-del-Solar, N. de la Rosa-Fox and L. Esquivias. "Basic Features of the Glassy State" Ed. J. Colmenero and A. Alegría (Singapore, 1990) p. 68.

Monte-Carlo-simulation of the glass transition in
three-dimensional dense polymer melts

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In this Monte-Carlo-simulation we model the polymer chains by self and mutually avoiding walks on a simple cubic lattice where each monomer occupies a *whole unit cell* and not only a single lattice site. Therefore a variety of bond-vectors (108 in total) are available for each bond whose lengths are chosen in such a way that no crossing of two bonds can occur during the course of the motion of the monomers. This so called "bond-fluctuation" model exhibits the expected static and dynamic features for dense polymer melts (i.e., $\langle R_G^2 \rangle \propto N$, Rouse behaviour). In order to introduce temperature and "frustration" into the model we put an energy of ϵ on each bond-vector unless it does belong to a specified class of bond-vectors. This class comprises the bond-vectors of length 3 and direction along one of the three lattice axis so that a single polymer should be totally stretched out in its ground state. In a dense polymer melt the competition between all chains prevents a single chain from reaching the energetically favoured expanded state. The effects of this "geometrical frustration" are exemplified by the dependence of various static quantities, such as the energy per bond, the compressibility of the melt or the radius of gyration of a single chain, on temperature. It is shown that this dependence is sensitively influenced by the choice of the quench rate. Five different quench rates, covering a range of two to three decades, were used for analysis of the static data. For some of these quench rates preliminary results for dynamic quantities, such as the diffusion coefficient or correlation functions, are presented. All results obtained up to now stress the fact that the used version of the bond-fluctuation model is well suited for the theoretical analysis of the glass transition and thus should be applicable for a critical test of the predictions of the various theories, such as the mode-coupling theory.

Is the soft potential model able to explain the glassy anomalies?

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The soft potential model (1) is an extension of the tunnelling model. It assumes a fixed effective mass and a random distribution of potentials for the tunnelling or vibrating entities.

Recently, the model has been developed to describe a number of the so-called low-temperature anomalies in glasses in a quantitative way. It turns out that one needs a relatively high effective mass, corresponding to about hundred atoms participating in a single tunnelling or vibrational mode.

We discuss the question to which extent the soft potential model enables a unified description of all the low-temperature glassy anomalies.

(1) V.G. Karpov, M.I. Klinger and F.I. Ignat'ev, Sov. Phys. JETP, **65**, 165 (1983).

THE STUDY OF CRYSTALLIZATION OF GLASSES
BY THERMAL ANALYSIS

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Although the general theory of crystallization kinetics is largely confined to the description of the isothermal transformation condition, there are many instances where the kinetic behavior of a system which is heated or cooled through the transformation region is of greater practical importance. From this point of view the methods of thermal analysis (TA) seems to be very useful techniques for obtaining kinetic information about the crystallization process. Nevertheless, there is still an open question: *How to determine correctly the kinetic parameters and how these parameters are affected by the instrumental factors and experimental conditions?*

A simple and consistent method of kinetic analysis of TA data has been developed. The method allows one to perform the correct determination of the most suitable kinetic model and subsequent calculation of all kinetic parameters needed for a quantitative description of the studied process. This method was used to study the kinetics of crystallization of chalcogenide glass measured by various TA instruments. The influence of instrumental factors is discussed with respect to the reliability of the kinetic parameters calculated from experimental TA data.

**RECENT RESULTS IN NEUTRON SCATTERING FROM
NON-CRYSTALLINE SOLIDS USING A PULSED SOURCE**

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Since the last conference, much experience has been gained and many interesting results have been obtained using the technique of pulsed neutron scattering. The advantages and unique properties of a pulsed source will be illustrated with results obtained on several of the instruments installed on ISIS at the Rutherford Appleton Laboratory, UK.

Diffraction experiments, which measure the structure factor, will be illustrated with results on conducting glasses, mechanical amorphization, quasi-crystals and amorphous carbon-hydrogen. Quasi-elastic and inelastic experiments, which provide information on the dynamics of the system, have been carried out on, for example, superionic glasses, the liquid-glass transition and amorphous hydrogenated carbon.

QUASIELASTIC NEUTRON SCATTERING STUDY OF THE DYNAMICS OF THE α -RELAXATION IN POLYMERS.

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We have studied the dynamics of the α -relaxation in different glass-forming polymeric systems, poly(vinyl methyl ether) (PVME), poly(vinyl chloride) (PVC), and poly(hydroxy ether of bisphenol-A) (Phenoxy, PH) by means of Incoherent Quasielastic Neutron Scattering. We have used the Backscattering Spectrometers IN10 and IN13 of the Institut Laue-Langevin (ILL) at Grenoble, France. In the energy windows of these spectrometers, the dynamics of the α -relaxation in the polymers investigated was detected as a quasielastic broadening at temperatures higher than approximately $T_g + 50^\circ$, T_g being the glass-transition temperature of the polymer considered. The quasielastic curves obtained cannot be well described by a single Lorentzian function. In order to fit these curves we have built a scattering function $S_{HN}(q, \omega)$ starting from the Havriliak-Negami relaxation function. Then, $S_{HN}(q, \omega)$ can be expressed as:

$$S_{HN}(q, \omega) \propto \frac{1}{\omega} \text{Im} \left[\frac{-1}{[1 + (i\omega\tau_{HN})^{\alpha\gamma}]} \right]$$

where α and γ are two shape parameters in the range ($0 < \alpha, \gamma < 1$) and τ_{HN} is a characteristic timescale depending on both, temperature and the modulus of the change of the wavevector, q . From the fitting procedure we obtain α and γ values as well as $\tau_{HN}(q, T)$. The results obtained indicate that $\tau_{HN}(q, T)$ can be factorized as $\tau_{HN}(q, T) = a(T) \cdot \check{\tau}(q)$. The q -dependence of τ_{HN} , $\check{\tau}(q)$, obtained for the polymers investigated can be described by a power law $\check{\tau}(q) \propto q^{-n}$ with an "anomalous" value of $n > 2$ in the q -range covered by us ($0.2 < q < 5.4 \text{ \AA}^{-1}$). The found value of n depends on the polymer considered. On the other hand, the values of the shape parameters α and γ found are close to the corresponding values obtained by relaxation techniques in a different time range ($10^{-6} - 10 \text{ s.}$). Moreover, the $a(T)$ behaviour deduced for each polymer investigated can be well fitted by the functional form describing the temperature behaviour of the H-N characteristic times measured by relaxation techniques in the same polymer.

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NEUTRON DIFFRACTION STUDY OF STRUCTURAL CHANGES INDUCED BY HEAT TREATMENT IN GE-SE GLASSES

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Glasses of $\text{Ge}_x\text{Se}_{1-x}$ with $x = 0.15, 0.20$ and 0.25 were prepared by melt quenching. The structural changes induced by heat treatment were analyzed with the instrument DIB at the Institute von Laue-Langevin in Grenoble. The aim of this work was to study the possible formation of metastable phases from the amorphous phase before the crystallization of the stable phases as has been previously reported.

The diffraction pattern ($2\theta \leq 80^\circ$) was recorded from room temperature up to about 700 K on heating at ~ 0.2 K/min followed by isothermal treatments and further cooling down. For the three compositions studied, at a certain temperature T_c , ($T_c = 520$ K for $x=0.15$) an orthorhombic metastable phase appeared in the diffractogram whose Bragg peaks first increased and then decreased on heating above a metastable liquidus temperature, T_{ml} ($T_{ml} = 600$ K for $x=0.15$). Some non-crystalline phase was always present at the same time than the metastable crystalline phase, irrespective of the heat treatment applied to the glassy sample. The decrease of the Bragg peaks was associated with an increasing of the non-crystalline background in the diffractogram. The values of T_{ml} increase with the Ge content and remain in the range 600-630 K, that is at temperatures lower than those of the stable liquidus temperature. On cooling the molten alloy with $x=0.25$ from ~ 700 K at about 0.4 K/min the metastable phase coexists with the stable monoclinic GeSe_2 , the amount of the last one increasing with decreasing temperature. The crystallization kinetics of the metastable phase has been deduced from the structural results.

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ON THE OPTICAL ABSORPTION IN AMORPHOUS As-S FILMS DEPOSITED BY THERMAL EVAPORATION

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The optical transmission spectra at normal incidence of amorphous As-S thin films prepared by thermal evaporation on room-temperature substrates have been measured over the spectral region of 0.3 to 2.0 μm . A simple procedure suggested by Swanepoel, which is based on the use of the extremes of the interference fringes, has been applied to determine the index of refraction, n , and the absorption coefficient, α , as well as the film thickness; independent thickness measurements made by surface-profiling stylus have also been carried out to cross-check the results obtained by the envelope method. Moreover, the dispersion of n is discussed in terms of the single-oscillator model ($n^2 - 1 = E_d E_o / (E_o^2 - \hbar^2 \omega^2)$), where $\hbar \omega$ is the photon energy, E_o is the single oscillator energy and E_d is the dispersion energy). On the other hand, the absorption edge is described on the basis of the non-direct transition model proposed by Tonc, whose relation for α has the form $\alpha \hbar \omega = B (\hbar \omega - E_g^{\text{opt}})^2$, and where E_g^{opt} is the optical band gap and B is an energy-independent constant. Finally, the relationship between the optical gap and the chemical composition is discussed, following Yamaguchi's approach, in terms of the average heat of atomization and the average coordination number.

SPECIFIC HEAT MEASUREMENTS OF GE DOPPED $\text{Te}_{15}\text{Se}_{85}$ GLASSES IN THE GLASS TRANSITION REGION

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The glass transition is a phenomenon which may easily be observed in most glasses by means of techniques such as differential scanning calorimetry (DSC). This is due to the fact that on heating (cooling) the heat capacity, C_p , of a glass increases (decreases) suddenly by at least about half its original value in the glass transition region. The dependence of the glass transition temperature on the heating rate employed for its measurement is a well known fact for most chalcogenide glasses [1] and has been extensively studied from a theoretical point of view as a relaxation phenomena [2,3]. Nevertheless the nature of the glass transition is a question that remains open.

Accurate measurements of the apparent heat capacity below and during the glass transition were performed by DSC on $\text{Ge}(\text{Te}_{15}\text{Se}_{85})_{1-x}$ glasses with $x = 0, 2$ and 10 . Isothermal and continuous heating annealings were performed both in as-quenched and in slowly cooled glasses. The enthalpy difference between each annealed glass and the undercooled liquid was taken as a property sensitive to the relaxation induced in the glass. An accurate description of both iso- and non-isothermal measurements was obtained by the activation energy spectrum model [4].

1. M.T. Clavaguera-Mora, M.D. Baró, S. Suriñach, J. Saurina and N. Clavaguera, *J. Non-Cryst. Solids* 131-133 (1991) 479.
2. G.S. Grest and M.H. Cohen, *Phys. Rev. B* 21 (1980) 4113.
3. M.T. Clavaguera-Mora, *Thermochim. Acta*, 148 (1989) 261.
4. M.R.J. Gibbs, J.E. Evetts and J.A. Leake, *J. Mater. Sci.* 18 (1983) 611.

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CRYSTALLIZATION OF $\text{Te}_{15}\text{Se}_{85}$ GLASSY ALLOY: CALORIMETRIC AND MORPHOLOGICAL STUDY

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The calorimetric study of the crystallization of a glass allows to obtain the kinetic parameters of the overall reaction [1]. The morphological study of the first stages of the crystallization process is very suitable to study the kinetics of nucleation and crystal growth separately. The twinning of both studies gives a complete description of the crystallization reaction.

The present work is concerned with the study of the crystallization behaviour of $\text{Se}_{85}\text{Te}_{15}$ air quenched glass. The study was made by differential scanning calorimetry (DSC), X-ray diffraction and optical and scanning electron microscopy. The calorimetric results show that there is only one stage of crystallization which is correctly described by the Johnson-Mehl-Avrami-Erofe'ev equation, with an Arrhenius form of the rate constant, under both isothermal and continuous heating conditions [2]. The isothermal crystallization process has also been studied by optical and scanning electron microscopy, using static observations at room temperature of different partially crystallized glassy alloys [3]. Crystallization takes place by nucleation and growth of individual crystals. The morphological analysis allowed to determine the nucleation and crystal growth rates and the activation energy for each process. The results obtained from the morphological study are in agreement with the calorimetric ones. From them the low temperature parts of the T-T-T and the T-HR-T curves have been deduced.

1. S. Suriñach, M.D. Baró, M.T. Clavaguera-Mora and N. Clavaguera, J. Non-Cryst. Solids 58 (1983) 209.
2. Y. Calventus, M.D. Baró, S. Suriñach, S. Bordas, M.T. Clavaguera-Mora and N. Clavaguera, Anal. Fis. B86 (1990) 134.
3. R.S. Tiwari, S. Ranganathan and M. Heimendahl, Z. Metallkde. 72 (1981) 563.

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Fe-57 MÖSSBAUER STUDY OF SOME $(\text{FeCo})_{75}\text{SiB}$ METALLIC ALLOYS

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In the last few years, different experiments have been carried out in (FeCo) containing metallic glasses. They provide strong evidence of the existence of Chemical Short Range Order in such alloys as well as the evolution of such order upon thermal treatments. Very recently, it has been shown there is a change on $(\text{Fe}_x\text{Co}_{1-x})_{75}\text{Si}_{15}\text{B}_{10}$ metallic alloy's Short Range Order (SRO) as function of x /1,2/. On the other hand, the saturation magnetostriction of the cited metallic alloys serie changes sign on the very Co rich side /3/. Direct insight on the local neighbouring of the Fe atoms can be obtained by means of ^{57}Fe Mössbauer Spectroscopy.

In this work we report measurements on $(\text{Fe}_{94}\text{Co}_6)_{75}\text{Si}_x\text{B}_{25-x}$, $(\text{Fe}_{50}\text{Co}_{50})_{75}\text{Si}_x\text{B}_{25-x}$ and $(\text{Fe}_{20}\text{Co}_{80})_{75}\text{Si}_x\text{B}_{25-x}$ metallic glasses in the composition range $0 \leq x \leq 20$ to understand the metalloid influence on the observed changes on SRO. We also report Mössbauer measurements on the Co rich side of the $(\text{Fe}_x\text{Co}_{1-x})_{75}\text{Si}_{15}\text{B}_{10}$ metallic alloy's series for positive and negative magnetostrictions.

/1/ M.L.Fdez-Gubieda, Thesis. Universidad del País Vasco (1991).

/2/ M.L.Fdez-Gubieda, J.M.Barandiarán, F.Plazaola, A. Hernando and S. Mobilio sent to J.Physics: Condensed Matter

/3/ A. Hernando, V. Madurga, J.M. Barandiarán and O.V. Nielsen, Solid State Comm. 54 (1985) 1059.

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**Magnetic and structural characterization of nanocrystalline
Fe-Cu-Nb-Si-B alloys.**

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As recently reported, some Fe-rich amorphous alloys with small additions of Cu and Nb atoms exhibit quite outstanding soft magnetic behavior after thermal treatments above crystallization temperature. This has been interpreted considering the formation of α -Fe ultrafine grain structure with typical diameter of 10-20 nm giving rise to vanishing macroscopic magnetocrystalline anisotropy according to random anisotropy model¹.

In the present work, thermal treatments were performed in a conventional furnace for a series of different temperature and time of annealing on $\text{Fe}_{73.5}\text{Cu}_1\text{Nb}_3\text{Si}_{16.5}\text{B}_6$ and $\text{Fe}_{73.5}\text{Cu}_1\text{Nb}_3\text{Si}_{13.5}\text{B}_6$ amorphous alloys. Alternatively, heating of the samples was also performed by making an electrical current flow along the ribbons (current annealing). Low frequency hysteresis loops and their typical magnitudes (coercive field, remanent and saturation magnetization, etc) have been measured as a function of the treatment parameters (current intensity, temperature and time). While treatments at around 540°C give rise to very soft magnetic behavior (i.e. coercive fields less than 10 mOe), annealing above 600°C deteriorate drastically such behavior (i.e. coercive fields larger than 10 Oe). Comparison between the effect of both kinds of treatments on the magnetic properties is reported. The different magnetic response to applied stress after different treatments, a consequence of the magnetostriction modifications, is also shown.

A parallel study on crystallization and structural characterization by differential scanning calorimetry and X-ray diffraction has been also done. Correlation between magnetic properties and microstructure is discussed.

1.- G.Herzer IEEE Trans. Magn. 26(1990) 1379

**MAGNETIC PROPERTIES OF TERNARY Co-B-C MELT SPUN
ALLOYS AMORPHIZED OVER
AN EXTENDED CONCENTRATION RANGE**

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ABSTRACT

The field dependence of the magnetization at 4.2 K, 294 K and the temperature dependence of the spontaneous magnetization for two series of ternary Co-based alloys, namely $\text{Co}_{76-x}\text{B}_{24}\text{C}_x$ and $\text{Co}_{88-y}\text{B}_y\text{C}_{12}$ have been measured. The metalloid content in these series ranges from 24 to 44 at.%, and extends almost to the critical concentration for the disappearance of ferromagnetism.

The composition dependence of the average magnetic moment at 4.2 K compares well, for low metalloid content, with data for other Co-based materials and also with the theoretical models that predict a linear dependence of the magnetic moment as a function of concentration.

The thermal demagnetizing process at low temperatures is presented. The results have been analyzed in terms of Bloch's Law although other contributions cannot be ruled out. The complete thermal demagnetization, i.e. down to T_c , is presented only for the alloys with a Curie temperature below 300 K. The results show the well known flattening of the $M(T)$ curve as compare with crystalline materials.

**MAGNETIC PROPERTIES OF RAPIDLY QUENCHED
NdDyFeB ALLOYS**

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ABSTRACT

The effects of wheel speed on the magnetic properties of melt-spun $\text{Fe}_{75}\text{Nd}_{13.5}\text{Dy}_{3.7}\text{B}_{7.8}$ alloys have been studied. For the different samples we have determined the Curie temperature, the dependence of the coercive field on the applied magnetic field and the low field ac-susceptibility. The effect of heat treatments on the magnetic properties will be also discussed.

PHASE DISTRIBUTION AND MAGNETIC PROPERTIES OF MELT SPUN Sm-Fe-Ti

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Recently new permanent magnets materials have been prepared based on new phases of the Sm-Fe-TM system¹. These new phases are usually produced by means of non-equilibrium techniques such as rapid quenching or mechanical alloying. As it is well known the hysteretic behaviour of permanent magnets materials is determined both by their magnetocrystalline anisotropy and by their microstructural characteristics. In this work, and aiming at the study of samples with the widest possible range of microstructures, we present results corresponding to samples of nominal composition $\text{Sm}_x\text{Fe}_{100-x}\text{Ti}_{10}$ ($x = 12, 16, 20, 24$ and 26) prepared by the melt-spinning technique, using different cooling rates in order to obtain different proportions of amorphous to crystalline phases. The phase distribution of the as-quenched samples was studied by means of X-ray diffraction. Amorphization is enhanced with the increase in Sm content although there is always a small amount of crystallites (1:12 phase) even for the highest cooling rate used during the quenching (measured through the tangential speed of the roller) and the highest Sm content. Magnetic characterization of the as-cast samples were performed by means of an extraction magnetometer by measuring the field for which the magnetization vanishes (after application of a maximum field of 12 T), the maximum coercive force and the demagnetization process around the remanence. As-cast samples exhibited different behaviour depending on their degree of amorphousness but, in general, magnetic hardness was not developed upon preparation. Samples with the highest amorphous phase content were annealed at temperatures between 750-850°C and for times in the range of 3-30'. Hysteresis loops of annealed samples are typical of a two magnetic phase material: the hardest magnetic phase presents an coercive force of 1.5 T, which is due to the presence of the 1:12 phase as it is shown by the X-ray diffraction patterns.

¹ M. Katter, J. Wecker and L. Schultz. Appl. Phys. Lett. **56** (14) 1377-1379 (1990)

SELECTION AND PROCESSING OF METALLIC GLASS
MATERIALS FOR FLUXGATE APPLICATIONS

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ABSTRACT

Many fluxgate magnetometers use as the magnetic sensing element the ringcore fluxgate. The sensing mechanism is based on the ability for the ferromagnetic core material to be fully AC magnetized by a moderate AC current flowing in the toroidally wound excitation coil.

The classical material used in the magnetic core consists of sheets or ribbons of the permalloy type. A serious drawback for this material is its high sensitivity to small mechanical stresses which makes a heat treatment necessary after the sensor production.

In recent papers it has been demonstrated that non-magnetostrictive metallic glass ribbons, suitably heat treated, compete favourably with traditional core materials of the permalloy type. In the present work we make a systematical study with the purpose of further reducing in the low noise level (about 17 pT, RMS 0.06-10.0 Hz) normally obtained as a standard for sensors from our present methods of production. The lowest noise level we have obtained till now is 12 pT for a sensor like those discussed below

VARIATION OF THE MAGNETIC ANISOTROPY OF AMORPHOUS RIBBONS BY
REDUCTION IN THICKNESS BY MECHANICAL POLISHING

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ABSTRACT

Magnetic anisotropy of low magnetostrictive Co-based alloys (VC-6150) has been measured by torque magnetometry for different thicknesses obtained by mechanical polishing of the as-quenched sample. The results allow us to evaluate the contribution to the whole anisotropy of the different possible origins such as surface roughness or induced anisotropies produced during the quench.

ANISOTROPY FIELD DISTRIBUTION IN AMORPHOUS Co-P ALLOYS

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As is well known, the amorphous Co-P alloys obtained by electrodeposition show high magnetic anisotropy with its easy axis perpendicular to the deposition surface. Such anisotropy has been related to the columnar growth of a Co rich phase during the alloy formation /1/. A procedure for obtaining the anisotropy distribution in ferromagnetic amorphous alloys has been recently developed /2/. In this work we report the study of the evolution of the anisotropy distribution as a function of the annealing temperature in some $\text{Co}_{1-x}\text{P}_x$ ($0.07 < x < 0.20$) alloys. For some alloys the anisotropy field and the width of the distribution decrease with the annealing before a huge perpendicular anisotropy is developed at cristallization. Other samples show the appearance of a clear assymetry in the distribution although at crystallization there is not a definite perpendicular magnetic anisotropy. These differences are related to the temperature and electrical current density involved in the preparation, that determine the estructure and composition of the samples.

- /1/ J.M. Riveiro, M.C. Sánchez and G.Rivero. IEEE Trans. on Magn. 17, 1282 (1981).
- /2/ J.M.Barandiarán, M.Vázquez, A.Hernando, J.González and G.Rivero. IEEE Trans. on Magn. 25, 3330, (1989).

UNIDIRECTIONAL MAGNETIC ANISOTROPY IN METALLIC GLASSES

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The existence of a weak unidirectional magnetic anisotropy has been recently observed in some metallic glasses (1). This anisotropy appears after an intense and constant magnetic field was applied to the sample. This anisotropy disappears if an intense alternating magnetic field is applied.

The origin of this magnetic anisotropy remain unknown, although there are indications that it could be related to the presence of clusters with high local magnetic anisotropy in the amorphous matrix (1). In this work we describe a method to measure the unidirectional magnetic anisotropy and its temperature dependence. This magnetic phenomenon was studied in the metallic glass $\text{Co}_{75}\text{B}_{25}$ up to crystallization temperature.

(1) J.M. Riveiro, U. Phys.: Cond. Matter 3, 3563 (1991)

LARGE BARKHAUSEN EFFECT AND COUPLING FACTOR IN AMORPHOUS WIRE MATERIAL

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Bistable behaviour occurs in highly magnetostrictive amorphous wires due to the presence of an inner core. The dependence of the magnetic parameters: (1) the switching field H^* , (2) coercive field H_c and (3) reduced remenence m_r , on applied tensile stress σ_a , has been studied in current annealed amorphous wires. The switching field increases as $\sigma_a^{1/2}$ in fully relaxed samples, while in both as quenched and partially relaxed samples the $\sigma_a^{1/2}$ relationship holds only at high values of σ_a . The coercive field increases with σ_a in a way similar to H^* and m_r increases up to the saturation value. This behaviour can be explained by taking into account the different regions that have been proposed for these wires. We also present data on the effect of length. The switching field increases with length up to a saturation value. A minimum of about 60 mm is needed for the occurrence of bistability. We conclude that the axial demagnetizing field which depends on inner core dimensions and stresses also determines values of the switching field.

We have also made the first dynamic coupling factor measurements in current annealed amorphous wires. The materials are very lossy at the resonant frequencies due to eddy currents. Values of the coupling factor are therefore lower than in static coupling factor measurements. Optimum current annealing conditions were established.

**STUDY FOR PHASE SEPARATION IN AMORPHOUS PEN/PET
BLENDS
BY MEANS OF ^{13}C CP/MAS NMR**

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CP/MAS/DD ^{13}C NMR has been demonstrated as a valuable tool for the characterization of polymer-polymer miscibility. In general, the mostly used methods are as: 1) Perturbation in the isotropic chemical shift; 2) Intermolecular CP in a mixture of deuterated and protonated materials; 3) Determine the proton relaxation times.

For some polymer blends systems, such as the systems report here, blends of poly (ethylene naphthalene-2,6-dicarboxylate) (PEN) and poly (ethylene terephthalate) (PET), the chemical shifts and even the proton relaxation times of the components are the same, so it is difficult to use the above methods to get information. Here we show that delay decoupling and no decoupling CP/MAS NMR methods can get information about the miscibility of the systems.

The polymers and the blends samples are dissolved in hexafluoroisopropanol and precipitated by ethanol. The amorphous blends are obtained.

For the four blends, 50 PEN/50 PET- d_8 blend, 50 PEN-co-PHB (60:40)/50 PET- d_8 blend, 50 PEN/50 PEN-co-PHB- d_{10} (80:20) blend, and 50 PET/50 PEN-co-PHB- d_{10} (80:20) blend, we measure the CP/MAS NMR spectra with no dipolar decoupling and delay decoupling, compare them with the normal CP/MAS/DD spectra, and find that:

1) Only for 50 PEN/50 PEN-co-PHB- d_{10} (80:20) blend, the intermolecular cross polarization between the deuterated carbons in PEN-co-PHB- d_{10} (80:20) and the protons in PEN are observed in the delayed decoupling and no decoupling ^{13}C CP/MAS spectra. This means that the average distances between deuterated-carbons in PEN-co-PHB- d_{10} (80:20) and protons in PEN in the blend is on the order of 10\AA or less, i.e. the system is sufficiently miscible on a molecular scale.

2) The delayed decoupling and no decoupling ^{13}C CP/MAS measurement is more useful than the normal ^{13}C CP/MAS/DD measurement, because by using the former method, there is no chemical shift and proton relaxation time range limitation of the components.

**STUDY OF THE MOLECULAR DYNAMICS IN PVME/PH MISCIBLE BLENDS
BY MEANS OF NUCLEAR MAGNETIC RESONANCE**

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We have investigated the molecular dynamics in a miscible (only one glass-transition process) glass-forming polymer system Poly(vinyl methyl ether)/Phenoxy (PVME/PH) by means of ^{13}C Nuclear Magnetic Resonance, i.e., in a mesoscopic time scale (10^{-7} - 10^{-10} s). The magnitude measured was the temperature behaviour of the ^{13}C spin-lattice relaxation time T_1 at a frequency of 75.4 MHz. The big advantage of NMR technique over other relaxation techniques is that ^{13}C NMR allow us to follow the relaxation behaviour corresponding to a given carbon. In our case we have followed the relaxation behaviour of both, CH group of PVME and the protonated carbon of the phenyl group of PH. This procedure gives the opportunity of studying how the dynamics of one of the components of the blend is affected by the presence of the other component.

With the assumption of a purely ^{13}C - ^1H dipolar relaxation mechanism T_1 is given by

$$T_1^{-1} = \frac{\pi^2 \gamma_C^2 \gamma_H^2}{10 r_{CH}^6} \left[3J(\omega_C) + 6J(\omega_H + \omega_C) + J(\omega_H - \omega_C) \right]$$

where ω_C and ω_H are the Larmor frequencies for carbon and proton respectively, γ_C and γ_H are the gyromagnetic ratios and r_{CH} is the carbon-proton internuclear distance. $J(\omega)$ is the spectral density function which is defined as the Fourier transform of the self correlation function $G(t)$ of the C-H relative orientation. In this work we have assumed a stretched exponential form for $G(t)$, $G(t) = \exp[-(t/\tau_c(T))^\beta]$. τ_c is a characteristic time scale and β is a parameter $0 < \beta < 1$ which gives account of the separation of $G(t)$ from a single exponential decay. The results obtained indicate that the correlation time $\tau_c(T)$ for the CH group of PVME and for the phenyl group of PH in all the PVME/PH compositions studied are similar. This support the idea of a dynamical miscibility in this system at least at the mesoscopic time range. On the other hand, we have obtained the variation of the β parameter values as well as the apparent activation energy values (from $\ln \tau_c$ versus $1/T$) for the CH group of PVME and for the phenyl group of PH, as a function of the blend composition. The behaviours obtained have been interpreted in the framework of the coupling model ideas.

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PHYSICAL AGING AND DIELECTRIC RELAXATION IN A POLAR GLASSY POLYMER.*

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Nowadays it is well known that a glassy polymer below the glass-transition is an unstable system which will have slow decay towards the supercooled liquid-like equilibrium state. This process, which is frequently called physical aging, can be monitored by means of thermodynamic magnitudes as volume or enthalpy. However, while this process is going on, other physical properties as the dielectric response in the case of polar systems, should also be affected.

In this work we have investigated enthalpy recovery and the change of the dielectric response as a function of the annealing time, just below the glass transition, in Poly(bisphenol A, 2-hydroxypropylether) (phenoxy). For the enthalpy recovery measurements a Perkin-Elmer DSC-4 set-up was used. For the dielectric relaxation study we used a time domain experimental procedure based on the transient current technique. In this experimental procedure, the sample is cooled down at constant rate, from above T_g , until the measurement temperature ($T < T_g$) is reached. After a given annealing time, the electric field is applied during a polarization time t_p . When the electric field is removed, the depolarization current is measured as a function of the time. The time behaviour of the current can be well described by assuming a stretched exponential functional form for the dielectric response function: $\Phi(t) = \exp[-(t/\tau_{WW})^\beta]$

The results obtained in this work indicate that physical aging produces a clear increase of the characteristic time scale τ_{WW} and a less clear variation of the exponent β . These results confirm previous ones obtained from other polymers. The comparison between enthalpic recovery and dielectric results allow to rationalize only some of the observed behaviours. Therefore, more insight effort from both, the experimental and theoretical points of view, is needed for a whole understanding of the dielectric behaviour.

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TEMPERATURE DEPENDENCE OF ENTHALPY RELAXATION PARAMETERS IN A FULLY CURED EPOXY RESIN

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A fully cured epoxy resin presents two characteristic aspects: The crosslinked nature and their glassy state. The chemical crosslink between functional groups gives the network structure and the thermosetting properties of the material. As a consequence of their glassy nature, epoxy resins can undergo structural relaxation or physical ageing at annealing temperatures below T_g , despite its network structure. The main goal of this work is the study of the temperature dependence of the ageing parameters in the enthalpy relaxation process of a fully cured resin, with a constant crosslinking density. The ageing parameters studied are enthalpy relaxation or relaxation function and the effective recovery time.

At low ageing temperatures (T_a) two endothermic peaks were detected by differential scanning calorimetry: one of them appears well below the glass transition (main peak), whose position and intensity is strongly dependent on ageing time t_a , and the other peak appears superposed to T_g (upper peak) with a very low intensity. The main peak is shown to be caused by the kinetics of the relaxation process, taking into account a distribution of relaxation times.

For each T_a , the enthalpy relaxation Δh increases with the annealing time and tends to have a limiting value which depends on T_a . This behavior is similar as such observed in thermoplastic polymers as a consequence of the segmental mobility decrease when the system approaches the equilibrium (metastable) state. This limiting value tends to increase with T_a till a maximum and further to decrease when T_a approaches to T_g . The maximum extent of the relaxation process has been observed at $T_a=80^\circ\text{C}$. Paralely the relaxation function $\phi(t)$ decreases exponentially with t_a and its decay increases gradually with T_a . The effective recovery time τ_{eff} increases with the extent of relaxation process because the segmental chains loss mobility. The variation of τ_{eff} with $\phi(t)$ decreases when T_a approaches to T_g .

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DILUENT EFFECT ON DYNAMIC MECHANICAL RELAXATIONS OF AN
AMORPHOUS COPOLYESTER

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The addition of plasticizers to polymers changes their mechanical properties, which can be adequately studied by means of dynamic mechanical analysis. The aim of this work is to study the influence on the viscoelastic behaviour of the diluent concentration in an amorphous copolyester based on poly(ethylene glycol terephthalate), and poly(1,4-cyclohexanedimethanol terephthalate) (3:1 by weight), plasticized with tricresylphosphate. Dynamic mechanical measurements were carried out at several frequencies in the temperature range from -140 to 120 °C, for several copolyester samples with varying concentration of diluent.

Two relaxations, alpha and beta in order of decreasing temperature, were found for the copolyester-diluent mixtures. They are differently affected by the concentration of the diluent. Thus, the intensity and sharpness as well as the temperature location of the former one, considered the glass transition of the plasticized samples, decrease as the amount of diluent increases. In contrast, the temperature location of the beta relaxation remains practically unaltered, although its intensity also decreases as the plasticizer concentration increases.

DYNAMIC MECHANICAL BEHAVIOUR OF VINYL ALCOHOL-ETHYLENE
COPOLYMERS

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The copolymers of vinyl alcohol and ethylene (VAE) with high concentration of the former component, are used increasingly as barrier layers for packaging foods and pharmaceuticals. These recent applications of materials synthesized long time ago have prompted the study of the structure-dependent properties of the VAE copolymers. The gas barrier properties of these materials are strongly affected by both vinyl alcohol and water contents, which can be studied by using different approaches, one of the most sensitive being dynamic mechanical measurements.

The analysis of the dynamic mechanical behaviour of the VAE copolymers has been done in connection with those corresponding to the related homopolymers, poly(vinyl alcohol) (PVA) and polyethylene (PE). The VAE copolymers show a viscoelastic behaviour more akin to that of PVA in the high temperature range, and similar to that of PE below room temperature. In this last range, a weak shoulder at -120 °C and a broad peak around -20 °C are found, which resemble the gamma relaxation of methylenic sequences and the beta relaxation of branched polyolefins, respectively. Moreover, the glass transition temperature of the VAE copolymers decreases as the ethylene content increases. The Tg's are clearly detected by dynamic mechanical analysis, in contrast to their difficult evidence in the DSC curves.

**LOCAL DEFORMATION INHOMOGENEITY IN DYNAMIC
MECHANICAL BEHAVIOUR OF BLOCK COPOLYMERS**

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Block copolymers forming domain structures are complex rheological bodies and their viscoelastic properties are far from being explained just on the basis of the properties of each component.

A model is presented which describes the relationship between macroscopic complex modulus and the distribution of local deformations in the sample in a wide temperature range. Some of these deformations are of large magnitude due to micromechanical stress concentration in an inhomogeneous system contrary to homogeneous one. Predictions of the model were compared with the experiments for a series of butadiene-styrene block copolymers and the predictions of our previously published model which described the contribution of interfacial layers. The relaxation spectra were analyzed as well.

NON-LINEAR CREEP AND THE EFFECT OF FREE VOLUMEN

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In recent work, it has been shown that, by a suitable generalization of the Cohen-Grest free volume theory, one could compute the order parameter and temperature dependence of a complete set of nematic viscosities for nematic polymers, either in equilibrium ¹, or in the out of equilibrium region close to the glass transition temperature ². We consider now the situation where the free volume depends on the applied stress. This dependence can easily be computed from our previous expressions, and a series of e.g. tensile creep curves can be computed. Our results are compared to experimental data on polypropylene and the agreement found is quite good.

1. A.C. Diogo, A.M. Velho - Mol. Cryst. Liq. Cryst. 153 (1987) 231.
2. A.C. Diogo, A.M. Velho - in "Molecular Structure and Rheology of Polymers",
Suppl. Rev. Port. Hemorr. (1990) (in press)

DETERMINATION OF TRAP PARAMETERS IN POLYMERS

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One of the main problems in the theory of thermally stimulated currents (TSC) is to take into account retrapping effects which take place during thermal release of trapped carries. For the sake of simplicity usually mode assumption is to neglect those effects, then one obtain formula first derived by Randall and Willmis.

In this paper an equation in generalized Randal - Willmis form was derived which takes into account retrapping phenomena.

THE STRUCTURAL RELAXATION BEHAVIOUR OF AMORPHOUS FeCrB

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Small amounts of transition metals strongly affect structural relaxation in FeB amorphous alloys [1]. Electrical resistivity measurements, both in isothermal and in scanning conditions, have been performed on $\text{Fe}_{75}\text{Cr}_5\text{B}_{20}$. Depending on the annealing temperature, both positive and negative values of the property changes as a function of time have been observed, suggesting that different types of short range ordering take place during relaxation.

Young's modulus variations (through velocity-of-sound measurements) have also been considered. In contrast with the resistivity measurements, in all cases a positive change is found for this property. For comparison, the same measurements have been performed on other iron-transition metal-boron glasses. A remarkable correlation between the resistivity changes and the relative Young's modulus changes is found.

Young's modulus measurements on pre-annealed samples disclose a reversible component in the structural relaxation.

[1] G.Riontino & F.Marino, Scripta Met. 18 (1984) 13

POSITRON LIFETIME AND X-RAY DIFFRACTION MEASUREMENTS DURING
STRUCTURAL RELAXATION IN METALLIC GLASSES $\text{Fe}_{78-x}\text{Co}_x\text{Si}_9\text{B}_{13}$

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The isothermal annealing of metallic glasses give rise to changes in many physical properties together with transition to the crystalline state in higher temperatures of annealing. The process is caused by atomic rearrangements in the amorphous structure and is generally called "structural relaxation".

Investigated specimens of metallic glasses $\text{Fe}_{78-x}\text{Co}_x\text{Si}_9\text{B}_{13}$ ($x=0,30,50,78$) were first preannealed for 10^5s at 530K and next the same specimens were further annealed at 578K and 778K (for 10^5s respectively).

The positron lifetime and X-ray diffraction measurements show that annealing process below the crystalline temperature (530K and 578K) causes changes in chemical and topological short range ordering. At the same time isothermal annealing at 778K causes increase in the number of positron - trapping voids and existence of α -Fe and β -Co crystalline phases.

CALORIMETRIC STUDY OF THE CRISTALLIZATION PROCESSES OF AMORPHOUS CoP ALLOYS

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Crystallization processes of amorphous alloys of composition $\text{Co}_{1-x}\text{P}_x$ ($10 < x < 25$) have been monitored through DSC measurements. Two different exothermic processes can be observed when the sample composition has a P content lower than the eutectic (20% atoms P), being the crystallization enthalpy, independently of composition, of 60 J/g for each process (when both peaks were not completely separable the global transformation enthalpy is approximately 120 J/g). The activation energy has been measured by performing several thermograms at different scanning rates, yielding values of 1.9 and 1.7 eV and frequency factors of the order of 10^{14} and 10^{11} s^{-1} for the first and second process respectively. X ray diffractograms of the final transformation product show peaks corresponding to Co (hcp + fcc) and Co_2P , whereas diffractograms of samples for which only the first stage of crystallization has been completed show the presence of Co plus an amorphous halo. Therefore, crystallization occurs through a two steps process: a primary transformation to Co plus a-CoP followed by a second crystallization, probably eutectic, of the remaining amorphous phase. Both the width of the XRD peaks and SEM observations of fresh fracture surfaces of the final product show that its microstructure is very fine, with maximum grain size of the order of 100 nm. Crystallization proceeds in a different way for the compositions with P content higher than the eutectic, in which a single exothermic process has been observed. In this case XRD also show Co and Co_2P peaks, with Co_2P presenting a strong texture, with the [001] direction perpendicular to the sample plane. Evaluation of the Co_2P grain size through the Scherrer expression gives a value of the order of 20 nm along the above mentioned direction.

CRYSTALLIZATION PROCESS BY STUDY OF RESISTIVITY THROUGH CONTROLLED JOULE EFFECT HEATING

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We have developed a new method of studying the crystallization process in melt-quenched amorphous magnetic alloys. This method consists of monitoring the resistivity while the amorphous sample (ribbon) is traversed by a current whose intensity is increased in a programmed way with time^{1,2}. Currents of intensities high enough to take the sample above the crystallization are employed. As a case study we report our results on $\text{Fe}_{80-x}\text{Ni}_x\text{B}_{12}\text{Si}_8$ alloys with $0 \leq x \leq 80$, prepared by melt spinning technique. Some interesting characteristics are observed as x is increased.

In this technique one observes the change in the resistivity (R) as a function of electric power (P), and steps are observed each time a phase transition occurs. Fig. 1 shows typical examples for $x=20$, 40 and 70 which are key compositions. After each stage of crystallization, x-ray analyses were made in order to identify the phase. From the analysis of the results some general conclusions have been drawn, which are briefly as follows:

At the time of vitrification the following local units are suggested to be present; a) Ni_3B , b) Ni_3Fe , c) Fe_3B .

In all the compositions studied the above appear either singly or as a mixture.

For $x=18$ and 36, if one considers the units (a) and (b) indicated above there remains 44 % of Fe in excess.

On the contrary for $x=69$, the crystalline phases are distributed between $\text{Ni}_{36}\text{B}_{12}$ (or Ni_3B), and $\text{Ni}_{33}\text{Fe}_{11}$ (or Ni_3Fe) and no excess of metal atoms appear.

1. R. Krishnan and P. Rougier, IEEE Trans. Mag. MAG 20 1370 1984

2. P. Rougier, Doctoral thesis, Paris VI, jan 1990

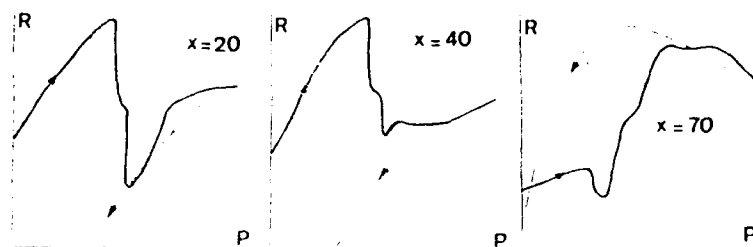


Fig. 1

**The Effect of Adding Ti and Zr on the Crystallization Behaviour of
Amorphous Fe-Cr-B Alloys**

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The crystallization behaviour of $\text{Fe}_{100-x-y}\text{Cr}_{18}\text{M}_x\text{B}_y$ ($\text{M} = \text{Ti}$ or Zr , $x=0-8$, $y=5-20$) amorphous alloy ribbons prepared by melt spinning have been investigated by a combination of differential scanning calorimetry (DSC) and transmission electron microscopy (TEM). Melt spun alloy ribbons containing Zr are amorphous over a wider range of chemical compositions than ribbons containing Ti. In continuous heating DSC experiments, the temperature of the exothermic crystallization peak increases and the heat of crystallization decreases in proportion to the Ti or Zr content, with a greater effect of Zr than Ti. In isothermal DSC experiments, the incubation time of the onset of crystallization obeys the Arrhenius law, the exothermic crystallization peak often obeys the Avrami law with an exponent of 3, and the activation energy for crystallization increases with addition of Ti or Zr. TEM examination of melt spun ribbons annealed just beyond the crystallization point shows fine scale microcrystalline microstructures consisting predominantly of α -Fe and $(\text{Fe,Cr})_3\text{B}$.

EFFECT OF NANOCRYSTALLIZATION ON THE ELECTRICAL RESISTIVITY OF AMORPHOUS $\text{Fe}_{73.5}\text{Cu}_1\text{Nb}_3\text{Si}_{13.5}\text{B}_9$ RIBBONS.

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Fe-based nanocrystalline metals obtained through proper annealings of amorphous ribbons may display excellent properties as soft magnetic materials. Initial permeability values as high as 100.000 have been obtained in nanocrystalline $\text{Fe}_{73.5}\text{Cu}_1\text{Nb}_3\text{Si}_{13.5}\text{B}_9$. The details of the amorphous to nanocrystal transformation in this system are rather unclear.

Electrical resistivity measurements have been performed by means of a four probe technique on $\text{Fe}_{73.5}\text{Cu}_1\text{Nb}_3\text{Si}_{13.5}\text{B}_9$ sample cut from a continuous amorphous ribbon obtained by planar flow casting in air. Isothermal measurements at temperature ranging between 485 °C and 535 °C show that the electrical resistivity is appreciably reduced during the development of a bcc nanocrystalline phase.

The resistivity decay is always a monotonic one; however no simple law is observed, indicating that the formation of nanocrystals is likely due to various diffusion processes.

Tempering measurements of the same property performed at 1 K/min and 6 K/min from room temperature up to about 700 °C, have been also considered for a kinetic analysis of the crystallization processes.

ON THE AMORPHIZATION OF THE SYSTEMS Nd-Fe AND Sm-Fe BY
MECHANICALLY ALLOYING.

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In the present work we study the amorphizability of the systems Nd-Fe and Sm-Fe prepared by the mechanical alloying technique, as well as the products formed after heat treatments. With this purpose, samples with nominal composition TR_xFe_{1-x} ($0.05 \leq x \leq 0.3$, TR = Nd, Sm) were prepared.

Basic characterization of the "as-milled" samples was performed by means of X-ray diffractometry. In the case of the Nd-Fe samples, after 64 h of milling time only peaks corresponding to Nd and α -Fe were visible. No diffuse halo was observed, probably indicating the absence of amorphous phases. On the other hand, on the Sm-Fe samples both a halo and α -Fe peaks were observed. This halo, whose intensity increases with the Sm content, can be associated to amorphous Sm-Fe phases. These differences in the ability for amorphization of both systems could be associated with the different value of the enthalpy of mixing.

Thermal stability was studied using a DSC, heating up to 730°C with a heating rate of 40°C/min. The intermediate phases (obtained by stopping the DSC scanning at a defined temperature before its completion) and the final products thus obtained were identified by X-ray diffractometry.

Magnetic characterization at room temperature of as-milled samples was carried out on small cylinders of pressed powder using a VSM. The measurements show that saturation magnetization decreases after milling if compared with the saturation magnetization values of unalloyed samples with the same Fe content. This fact be related to the alloying of the Nd and Sm, at least partially, with the Fe or formation of some other magnetic phases.

CORROSION BEHAVIOUR OF Fe₆₀Ni₂₀B₂₀ AMORPHOUS ALLOYS
PARTIALLY CRYSTALLIZED

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The study of the corrosion in amorphous metallic alloys has an increasing interest during the last years, because the amorphous alloys are also potentially attractive materials for electric motors, audio and video recording heads, magnetic shielding sheets and for building various electric and electronic devices(1,2).

In some applications, amorphous alloys must work at moderate temperature for long times. However, amorphous alloys are intrinsically unstable and leads to significant changes in their oxidation behaviour (4,5).

We present here the experimental results obtained using when the metglass ribbons were crystallized by an electrical current flows. The percentage of crystallinity was obtained by determination of the initial magnetic susceptibility. The electrochemical behaviour of the ribbons with different degree of crystallinity was followed by cyclic voltammetry. The studied metglas were Fe₆₀Ni₂₀B₂₀. As electrolyte, a KOH aqueous solution was employed.

Thick oxide layers were obtained when the metglass ribbons were subjected to consecutive potential sweeps between different anodic and cathodic potential limits. The oxide growth was followed stopping the consecutive sweeps and checking the voltamperometric response when the electrode was submitted to a potential sweeps between -200 and -1.200 mV at 200 mV/s.

- 1.- N.D. Cristofaro et al., J.Metals 38,1,(1986)
- 2.- H. Warlimont, as Ref. 1. p.1599 (1985)
- 3.- Gao Wei and B.Cantor, Ac. Metall. vol.36, n°8 2293-2305 (1988)
- 3.-R.S. Biassi, A.A.R. Fernandes, J.of Mater. Sci. 24, 14-44 (1989).

THERMAL STABILITY AND QUENCHING RATE OF AN FeSiB GLASS^(*)

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Metallic glasses are obtained by rapid quenching from the melt and so are metastable materials. Quenching rate is an important parameter affecting structure and glass temperature of the material of a composition.

In this paper we have studied the thermal stability of an Fe-based glass as a function of the gas pressure injection of the melt on the wheel during preparation of the ribbons. Differential scanning calorimetry (DSC) and thermal magnetogravimetry (TMG) measurements have been used in the study of Curie temperature and crystallization features of the alloys.

Devitrification transformation shows two stages but some changes at the onset and the interval between the two stages have been observed. Curie temperature and crystallization onset rise as long as thickness increases. Influence of the quenching rate on kinetic parameters is described.

^(*)Work supported by the C.I.C.Y.T. of the Spanish Government (Project MAT 88-301) and by the Junta de Andalucía.

RELAXATION BEHAVIOUR OF CURIE TEMPERATURE OF AN Fe-BASED GLASS^(*)

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Changes in the glassy state produced by annealing of metallic glasses below glass temperature, the so-called structural relaxation, affect many physical properties. One of the most sensitive properties to relaxation is the Curie point, T_c . For Fe-based glasses the reported results indicate that T_c rises to a saturation value after isothermal annealing. However, the time response of T_c and the dependence of its saturation value on the annealing temperature show compositional dependence, not yet well established.

In this contribution, the relaxation behaviour of a glass with nominal composition $Fe_{79}Si_{13}B_8$ is reported. DSC results show two crystallization stages: in the first, a precipitation of α -Fe occurs and during the second stage a polymorphic reaction gives α -Fe and Fe_2B phases as final products. The Curie temperature for the as-quenched alloy is 695 K and the crystallization onset is 835 K.

For all annealing temperatures in the explored range (720-750 K) T_c increases upon structural relaxation and ΔT_c is a monotonic function of annealing time and temperature. The saturation value, $T_c(\infty)$, rises with the annealing temperature, T_a , and $\Delta T_c(\infty)$ shows a linear dependence with $1/T_a$. Values of ΔT_c for each annealing temperature obey approximately a $\ln t$ law. The analysis of the experimental data in terms of a single relaxation time exponential equation yields, as expected, a relaxation time decreasing with increasing annealing temperature.

^(*) Work supported by the C.I.C.Y.T. of the Spanish Government (Project MAT 88-301) and by the Junta de Andalucía.

**ELECTRON MICROSCOPY STUDY OF CRYSTALLIZATION OF A
 $\text{Ni}_{68}\text{Cr}_{14}\text{B}_{18}$ GLASS^(*)**

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Amorphous to crystal transformation of the $\text{Ni}_{68}\text{Cr}_{14}\text{B}_{18}$ consists, at least, of two stages. DSC records, at a constant heating rate, show two overlapped exotherms and the crystallization onset (at 10 K/m) is 690 K. The kinetics of the non-isothermal transformation have been studied by deconvolution of the two exotherms.

Microstructural characterization has been carried out by electron microscopy using a Hitachi H800 microscope operated to 200 kV. The samples were thinned by ion-beam (Ar) or electrolytically (perchloric + acetic bath). Two types of samples were studied: partially or fully crystallized inside the calorimeter chamber prior to thinning and amorphous.

Three crystalline phases have been identified: an orthorhombic Ni_4B_3 type, an hexagonal Ni_7B_3 type and a cubic Ni type, respectively. Differences between crystallized samples prior to thinning and those crystallized inside the microscope are reported.

^(*)Work supported by the C.I.C.Y.T. of the Spanish Government (Project MAT 88-301) and by the Junta de Andalucía.

CRYSTALLIZATION KINETICS OF A $\text{Fe}_{75}\text{Co}_4\text{Si}_3\text{B}_{18}$

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We have studied the devitrification kinetics of an $\text{Fe}_{75}\text{Co}_4\text{B}_3\text{Si}_{18}$ alloy by means of calorimetric (DSC) methods. The non-isothermal DSC records show up to four exotherms for low heating rate values in the explored temperature range (300-1000 K). The crystallization onset occurs to 775 K and the higher enthalpy corresponds to the lower temperature exotherm resulting from overlapping of two peaks. Kinetics analysis have been derived from non-isothermal data and, for the main exotherm, by deconvolution of the overlapped maxima isothermal DSC records.

Microstructural characterization by electron microscopy is in progress.

X-RAY DIFFRACTION IN GLASSY POLYMERS AROUND T_g

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Since a long time the "Glass Transition" phenomenon is well known for polymers and other glasses. The mean square value of the density fluctuations has been studied by SAXS (Small Angle X-ray Scattering) for various amorphous polymers around the Glass Transition temperature (T_g). Its temperature behaviour is linear, with higher slope in the liquid ($T > T_g$) region than in the glassy ($T < T_g$) one, being the change of the slope located in T_g . Nevertheless, up to now no systematic studies have been developed by WAXS (Wide Angle X-ray Scattering) in order to know how the medium range order of polymeric glasses varies with the temperature around T_g .

In this work, WAXS patterns have been obtained at different temperatures between $T_g - 50K$ and $T_g + 50K$ for two amorphous polymers: Poly(Vinyl Acetate) (PVAc) and Poly(2-Hydroxypropylether of Bisphenol-A), Phenoxy, with T_g located around 313K and 373K respectively. We have paid our attention to the evolution with the temperature of the position and the intensity of the WAXS maxima obtained in the medium range order region for values of the scattering vector $s < 2.5 \text{ \AA}^{-1}$. These maxima are interpreted in terms of interchain correlations in the polymer. At room temperature, PVAc shows two high intensity maxima in this region located at 1 \AA^{-1} and 1.55 \AA^{-1} and Ph shows a high intensity maximum at 1.22 \AA^{-1} and a less intense one at shorter s values around 0.5 \AA^{-1} .

The results obtained at different temperatures show linear variations of the positions and the intensities of the maxima against the temperature. In the case of PVAc, the variation of the position shows different slopes below and above T_g (higher at $T > T_g$) for the first maximum; although no break in the temperature behaviour is found for the second one. This fact indicates the different origin of the two interchain correlations. Diffraction patterns obtained in oriented PVAc go in the same idea. In the case of Phenoxy, the temperature behaviour of the two peaks show the break located in T_g . Finally, Radial Distribution Functions have been obtained for the two polymers at different temperatures; no definite changes can be observed. A more definite conclusion in this section would need experimental results with better statistics.

This work has been carried out in the frame of the "Acciones Integradas Hispano Británicas" 34 and 96A and is supported in part by CICYT-project MEC MAT89-0186. Two of us (JJdV and JC) are grateful to the Gipuzkoako Foru Aldundia for partial financial support.

A NEW APPROACH TO THE STRUCTURAL STUDY OF NON CRYSTALLINE POLYMERS THROUGH NEUTRON DIFFRACTION

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The local structure of non crystalline polymers is largely unknown because of a multitude of possible intrachain and interchain correlations. It is difficult to separate these interactions which overlap in real and reciprocal spaces, particularly in polymeric materials containing substantial side groups pending from the backbone chain. In this work, we present a novel approach to the problem using a selective deuteration of the polymer chains in order to reveal the differing and complex interactions in non crystalline polymers.

We have used samples of glassy atactic polystyrene (PS) where the side group and the polymer backbone have been selectively deuterated. Four different PS samples were used: undeuterated PS (D0), PS deuterated only in the backbone chain (D3), PS deuterated only in the side group (D5), completely deuterated PS (D8). Wide Angle Neutron Diffraction data were obtained using both D20 instrument at ILL and SANDALS instrument at ISIS.

The inelasticity effects are easily observed in highly hydrogenated samples. In essence, these problems have been solved with relatively simple background and scaling operations. Such data may be in part directly analyzed and it is possible to advance some partial structure factor correlations which relate to specific site (e. g. polymer backbone-polymer backbone). In these pair correlation functions, the pairs are formed by specific structural units not atoms. These specific correlations are tested and compared to scattering functions obtained by computer built models. This powerful technique has considerable potential in the study of complex macromolecular materials.

This work has been carried out in the frame of the "Acciones Integradas Hispano Británicas" 34 and 96A. We are indebted to Dr. B. Frick (ILL) and to Dr. A. K. Soper (ISIS) for the aid during the experimental times and one of us (JJdV) is grateful to the Gipuzkoako Foru Aldundia for partial financial support.

NEUTRON SCATTERING STUDY OF CHAIN CONFORMATIONS IN THE MIXTURES OF BLOCK COPOLYMERS

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Mixtures of two-block copolymers form perfect common domain structures in a wide range of polydispersity and composition. Variation of the mixture composition and the relationship between molecular weights of the components allow to control the parameters of the structure.

With the aid of small-angle neutron scattering there were studied the conformations of polybutadiene chains in the binary mixtures of polystyrene-polybutadiene lamellae-forming block copolymers of different molecular weight. It was shown that the mixtures formed perfect common lamellae structures. The radius of giration R_g was measured about the normal to the interfaces. The R_g of long chains in the mixture depended on the concentration of short chains. For studied samples it varied from $0.59R_{g0}$ (R_{g0} is a calculated value for Gaussian coil) when the concentration of short chains was zero up to $0.82R_{g0}$ when each long chain was surrounded with about five short ones. The obtained data were compared with the theory concerning with chain conformations in the mixtures of block copolymers.

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MOLECULAR DYNAMICS IN PVAc AS STUDIED BY RELAXATION TECHNIQUES AND PHOTON CORRELATION SPECTROSCOPY.*

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A comparative study on the α -relaxation of poly(vinyl acetate) PVAc (Aldrich-Chemie 18.949-9) by means of different dynamic relaxation techniques and quasielastic light scattering (photon correlation spectroscopy, PCS) is presented here.

The PCS measurements were performed with an argon ion laser (model 95 Lexel) operating at a wavelength of $\lambda = 514.5$ nm with a power of 150 mW. Intensity autocorrelation functions were measured in the time range 10^{-6} - 10^0 s on a Malvern K7032 correlator. The temperature range measured was from 45 to 65°C ($T_g = 40$ °C). PCS results have been analyzed by assuming a stretched exponential functional form for the autocorrelation function of the scattered field:

$$g(t) = \exp[-(t/\tau)^\beta] \quad (1)$$

where β is a shape parameter and τ is a characteristic time scale.

Dynamic mechanical measurements were carried out on a DMTA Polymer Lab. apparatus. The complex mechanical modulus, $E^* = E' + iE''$, was recorded in the frequency range 10^{-2} - 10^2 Hz. at isothermal conditions. The temperature range covered was from 30 to 50°C. Dielectric spectroscopy measurements were performed scanning the frequency in the range $5 - 10^5$ Hz at isothermal conditions between 40 and 90 °C. On the other hand, NMR experiments were carried out by means of a Varian VXR-300 spectrometer. Carbon spin-lattice relaxation times T_1 and $T_{1\rho}$ were measured at 75.4 MHz and 35.3 kHz respectively in the temperature range 80 - 200 °C.

The relaxation results in the frequency domain were fitted with the Havriliak-Negami function:

$$\Phi^*(\omega) = \frac{1}{[1 + (i\omega\tau_{HN})^\gamma]^\gamma} \quad (2)$$

which was finally interpreted in terms of the stretched exponential time decay Eq.(1). The connection between both descriptions was previously reported (F. Alvarez et al., Phys. Rev. B **44**). In this way we are able to parametrize all the results in terms of the β and τ parameters. This procedure allows us to investigate a wide dynamical range through different spectroscopies.

* This work has been supported by the CICyT (project: MEC MAT89-0816) and by Gipuzkoako Foru Aldundia. One of us (FA) acknowledges the grant of the Basque Department of Education.

INFLUENCE OF THE STRETCHING ON THE MOLECULAR DYNAMICS OF GLASSY POLY(VINYL CHLORIDE)

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In the last years, the conformational microstructure of Poly(Vinyl Chloride) (PVC) has been shown to play an important role in the majority of its physical and chemical properties; moreover, the microstructure of PVC has been correlated to the molecular dynamics in the Glass Transition region. On the other hand, local conformational changes produced by the orientation of PVC chains (mainly, isotactic GTTG⁻ triads are transformed in isotactic GTTT triads) have been recently determined by means of FTIR spectroscopy. In this way, we have begun to study the influence of the stretching on the molecular dynamics of PVC, with the purpose of correlating conformational changes with molecular motions.

In this work, we present the results obtained by dynamic dielectric spectroscopy in non stretched and stretched isotactic PVC. These data are completed with DSC and WAXS results. Prior to all measurements, stretched samples were heated to temperatures above the Glass Transition one (T_g) in order to eliminate the deformation produced during the orientation process; in this way the results must only be related to the above mentioned conformational changes which are conserved even at temperatures $T \geq T_g$. Real and imaginary parts of the dielectric constant have been measured between 100K and 400K in a frequency range between 1Hz and 10^5 Hz. α (cooperative mobility at $T \geq T_g$) and β (local mobility) relaxation processes are measured in this temperature range.

α relaxation data, corrected from AC conductivity and from the influence of the β process which is very broad and overlapped to the α one, have been fitted to the Havriliak-Negami empirical distribution function and the relaxation time shows a Vogel-Fulcher temperature behaviour. No systematic differences between the samples in the parameters characterizing α relaxation confirm our previous ideas suggesting that the dynamics of PVC at $T \geq T_g$ is mainly driven by the tacticity distribution which is not altered by the orientation. In contrast, β relaxation results show strong differences between the samples: the temperature of loss peaks is lowered, the activation energy characteristic of the process is reduced by half and the intensity of the relaxation is increased. Our previous ideas suggesting that the local isotactic GTTG⁻ triad conformations have a great influence on the local molecular mobility at $T < T_g$ seem to be now confirmed.

Three of us (AE, JJdV and JC) thank Gipuzkoako Foru Aldundia for partial financial support.

STUDY OF THE EFFECT OF TEMPERATURE ON THE AMORPHOUS PET RELAXATIONS BY TSC.

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It has been studied the effect of temperature on PET-A using thermal annealing and the technique of progressive crystallization called Thermal Stimulation by Steps (TSS). The analysis of the spectrums of samples corona charged and afterwards discharged in open circuit show three peaks: α , ρ^* y ρ .

The peak ρ increases as the field does and has homopolar character which indicates that it is a peak due to free charge; and the discharges of electrets polarized only during the isothermal step show that it disappears at a temperature of polarization (T_p) of 100°C which results in a temperature of the maximum (T_m) of 105°C. The second peak, ρ^* , appears at 87°C and it has a strong heteropolar character; its origin is not well established although the mechanism has uniform character. The α relaxation increases as T_p does so that for high T_p it overlaps ρ^* and they seem to form a single peak. In a short circuit discharge ρ^* overlaps ρ relaxation.

The annealing of the samples at $T_a < T_g$ results in a decreasing of the intensity of ρ^* , so that if the time of annealing (t_a) is long it becomes homopolar, being greater the charge accumulation when the sample is negatively biased. As t_a increases, the T_m of ρ relaxation shifts to 105°C. For temperatures $T_a > T_g$ ($T_a = 87^\circ\text{C}$), the annealing results in a bounded decreasing of α and a sigmoidal increasing of ρ^* which indicates that the latest is related to the process that causes the nucleation; on the other hand ρ become wider and its T_m shifts to higher values.

The current that causes the inversion of ρ^* is connected to a mechanism that seems to be associated to the amorphous portion of the polymer, because its effects are less important as the degree of crystallinity increases (TSS), and it has been justified by the fact that the temperature creates trapping centers in the bulk and surface of the material, process that shows controversies that we reflect and discuss versus the effect of annealing.

THE GLASS FORMING ABILITY IN Cu - As - Se SYSTEM

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The glasses with chemical composition $\text{Cu}_x(\text{As}_{0.4}\text{Se}_{0.6})_{1-x}$ for $x = 0.0217, 0.0543, 0.065, 0.076, 0.1304$ and 0.239 were prepared. The kinetics of crystallization was investigated using heat flux DSC method. Basic kinetic parameters characterizing the crystallization process were determined.

The attention was also paid to the study of the compositional dependence of the glass transition temperature (T_g) as well as to the corresponding heat capacity change. It is shown that despite a considerable increase of mean coordination number with the increasing concentration of Cu, the T_g remains practically unchanged. It is shown that Tanaka's approach [1] seems not to be acceptable for these glasses. Nevertheless, it was found that using modified DeNeufville-Rockstad approach [2] the value of T_g can be well correlated with the coordination number and average atomization enthalpy of these glasses.

Following recent results of paper [3] the glass forming ability of Cu-As-Se glasses was calculated and compared with compositional trends of Hruby's [4] and Saad and Poulain [5] criterion. A new empirical criterion to describe the glass forming ability is also proposed.

- [1] K. Tanaka, Solid State Commun 54 (1985) 867.
- [2] J.P.DeNeufville and H.K.Rockstad, "Amorphous and Liquid Semiconductors 73, eds. J.Stuke and W.Brenig", Taylor and Francis, London (1974) p.419.
- [3] J.Málek, J. Non-Cryst. Solids 107 (1989) 323.
- [4] A.Hrubý, Czech. J. Phys. B22 (1972) 1187.
- [5] M.Saad, and M.Poulain, Mat. Sci. Forum 19-20 (1987) 11.

**ON CURRENT CONTROLLED DIFFERENTIAL RESISTANCE
IN CHALCOGENIDE GLASSY SEMICONDUCTORS.**

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Current Controlled Negative Differential Resistance (CCNDR) effect, typical of NTC thermistor behaviour, has been studied in bulk glassy chalcogenide semiconductor $\text{Cu}_{0.05}\text{As}_{0.50}\text{Te}_{0.45}$, obtained by the melt-quench method. This phenomenon has been explained in terms of a thermal model, where non-ohmic effects are excluded. The key lies in the balance of Joule self-heating, with the heat loss due to temperature difference with the ambient. As current increases step by step, the voltage measured at thermal equilibrium is lower than the ohmic value corresponding to constant resistance (dynamic resistance decreases when the temperature of the material increases), until a maximum voltage value (turnover voltage) is reached. From this point, steady state I-V characteristics of the semiconductor show a negative differential resistance region.

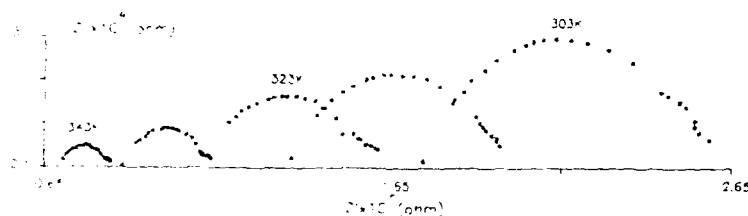
Electrode arrangement used to obtain these measurements, was made up of two copper discs, stuck on the polished semiconductor surface by applying silver paste. The interelectrode distance was measured from the microphotographs of the sample surface. Dependence of turnover voltage on ambient temperature was already studied from the point of view of a thermal model, showing good agreement. In this work, the relationship between turnover voltage and interelectrode distance has been studied, confirming the thermal nature of this physical process, and the absence of non-ohmic effects in the mechanism of electrical conduction.

ELECTRIC CONDUCTIVITY IN THE IONIC SOLID $\text{As}_{20}\text{Se}_{40}\text{Ag}_{40}$

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The calcogenide glasses of the As-Se-Ag system with a silver content show polarization phenomena which result in an ionic conductivity component. The measurements were carried out with a.c. on a graphite/glass/graphite cell at different temperatures by the complex impedance method[1] in the range of 60Hz to 70KHz a lock-in amplifier (5140, E.G.G.).

The graphic representation of the real part, Z' , versus the imaginary part, $-Z''$, at different temperatures (Fig.1) shows in each of them the characteristic circular arc of ionic solids. In the graph one can observe an arc belonging to the high frequency corresponding to the bulk and smaller one at low frequency due to grain boundary effects. The extrapolation in the low frequency zone up to the intersection with the real axis, of the arc corresponding to the bulk, makes it possible to know the conductivity.



In the range of the temperatures studied (30°C-100°C), the conductivity values, the activating energy and the preexponential factor -the last two obtained by least-square fitting- are presented in the following table:

| T | 303 | 313 | 323 | 333 | 343 | 353 | K |
|---|------|------|------|------|-------|-------|--|
| σT | 2.93 | 3.99 | 5.25 | 7.50 | 10.15 | 13.21 | $\Omega^{-1}\text{cm}^{-1}\text{K} \times 10^{-1}$ |
| $\Delta E_a = 0.30 \text{ eV} \quad \sigma_a = 1.35 \times 10^{-2} \Omega^{-1}\text{cm}^{-1}\text{K}$ | | | | | | | |

The equivalent circuit may be represented by RC parallel elements connected in series[3], and the centers of the arcs being below the real axis, suggests the existence of diffusion processes. Hence the Warburg impedance will be present in to the circuit[3]

REFERENCES

- [1] J.E. Bauerle, J.Phys.Chem, Vol.30, pp 2657-2670 (1969)
- [2] J.R. MacDonald, J.Chem.Phys. 61 (1977) 3977.
- [3] A.K. Jonscher, Nature 267 (1977) 573.

CHARACTERIZATION OF Se-BASED CHALCOGENIDE ALLOYS BY MEASUREMENT OF T_g VARIATIONS

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Many works try to link the values of the glass transition temperature T_g of disordered materials to physical parameters such as melting temperature [1], band gap [2] or average coordination number [3]. Although, for a given material, the value of T_g depends on preparation method, thermal history,... and could not be considered as a constant which characterizes the material.

In this paper we show that, for different vitreous selenium-based alloys, such as Se-Te, Se-Ge and Se-As, the variations of T_g with heating rate, measured by differential scanning calorimetry, follow an Arrhenius law. For a given alloy, the experimental results show that the activation energy does not depend on thermal history and is weakly dependent on preparation method. Finally, we show that this activation energy is characteristic of the nature of the atoms added to selenium as well as of the alloy composition.

[1] S. Sakka, J.D. Mackenzie, J.Non-Cryst. Solids 6 (1971) 145.

[2] J.P. De Neufville, H.K. Rockstad, Proc. 5th Int. Conf. Amorphous and Liquid Semicond., Ed. by J. Stuke and W. Brenig (Taylor and Francis, London, 1974) p.419.

[3] K. Tanaka, Solid State Commun. 54 (1985) 867.

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EVIDENCE OF TWO AMORPHOUS PHASES IN GE-TE-SB ALLOYS

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Ge-Te-Sb alloys, near the binary eutectic $\text{Ge}_{15}\text{Te}_{85}$, may be obtained in bulk amorphous form by quenching from the melt [1]. This paper reports the results obtained on $\text{Ge}_{15.5-x}\text{Te}_{84.5}\text{Sb}_x$ amorphous alloys ($0.5 < x < 2.5$) by differential scanning calorimetry. In this composition range we observe two glass transition temperatures T_{g1} and T_{g2} as well as two crystallization temperatures T_{C1} and T_{C2} , such a $T_{g1} < T_{g2} < T_{C1} < T_{C2}$ (table below), which is not the case for other Te-based amorphous alloys.

| x | 0.5 | 1.0 | 1.5 | 2.5 |
|---------------|-----|-----|-----|-----|
| T_{g1} (°C) | 120 | 116 | 114 | 108 |
| T_{g2} (°C) | 144 | 148 | 150 | 132 |
| T_{C1} (°C) | 174 | 166 | 168 | 160 |
| T_{C2} (°C) | 212 | 206 | 200 | 189 |

X-ray analysis of the alloys annealed above the first crystallization temperature show that the tellurium, in the hexagonal form, precipitates and that above T_{C2} , GeTe peaks appear in the diffraction diagrams. Further analysis by EXAFS could be able to specify both amorphous phases.

[1] P. LEBAUDY *et al.*, Materials Sci. & Eng. A 312 (1991) 273

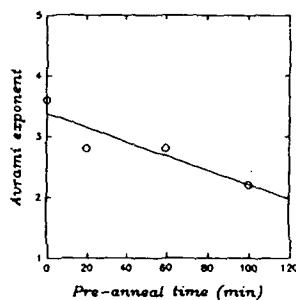
* permanent adress : Université Es-Sénia Oran Algérie

EFFECT OF ANNEALING ON AN AMORPHOUS $\text{Cu}_{0.03}\text{Ge}_{0.20}\text{Te}_{0.77}$ ALLOY.

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An isothermal pre-anneal treatment ($T = 453 \text{ K}$) was introduced to a quenched $\text{Cu}_{0.03}\text{Ge}_{0.20}\text{Te}_{0.77}$ glassy alloy.

By non-isothermal crystallizing the as-quenched and pre-annealed samples in a differential scanning calorimeter at five different heating rates (2, 4, 8, 16 and 32 K/min), the set of kinetic parameter which best describes the process (Avrami exponent, n , activation energy, E , and frequency factor, K_0) were obtained by using the Augis-Bennet technique [1].



It was found that the crystallization temperature and the Avrami exponent decreases systematically as the pre-anneal time increases, and the Avrami exponent tends to a certain value about 2 as shown in the figure.

In the pre-anneal treatment of the as-quenched material the density of pre-existing nuclei increases with the pre-anneal time, so that in the crystallization process, the nucleation rate would be slowed decreasing the values of Avrami exponent.

[1] J.A. Augis & J.E. Bennet, *J. Thermal Anal.*, 13 (1978) 283.

OPTICAL PROPERTIES OF Ge Sb THIN FILMS

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Electrical, Thermodynamic, and structural properties of the simple eutectic $Ge_{(1-x)}Sb_x$ system have been studied (1-4). However no optical properties have been studied in such a system. In this work we show the optical properties of thin films of amorphous $Ge_{(1-x)}Sb_x$ ($x = 68, 73, 84 \text{at.}\%$). The films were grown in a dc-magnetron sputtering system. Transmittance and Reflectance at normal incidence were measured in a Cary 17D spectrophotometer. The optical constants (n, k) and film thickness were found using the method described in ref.(5) in the spectral range 400-2500 nm.

The absorption α depends on the stoichiometry of the film, and the higher the Sb content of the film is, the higher the absorption is (Fig.1). In the region near the edge of absorption, α can be described by the relation

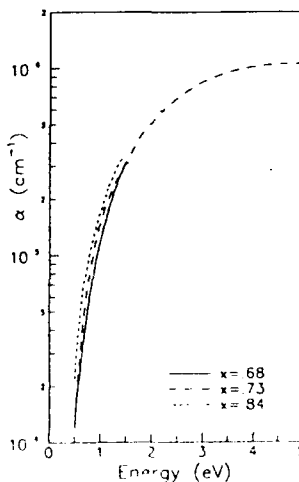
$$h\nu\alpha \propto (h\nu - E_g)^2$$

The optical band-gap, E_g , also depends on the stoichiometry, and the values obtained were:

| | | | |
|------------------|-----|-----|------|
| Sb(%at.) | 68 | 73 | 84 |
| $E_g(\text{eV})$ | 0.5 | 0.4 | 0.37 |

In the 68at.%Sb film the band tail, characteristic of amorphous semiconductors, was found. In the other compositions no band tail appear in the studied spectral region.

- [1] N. Croitoru, Thin Solid Films 44, L19 (1977).
- [2] S. B. Field and T. F. Rosenbaum, Phys. Rev. Lett. 55, 522 (1985).
- [3] P. Y. Chevalier, Thermochim. Acta 155, 227 (1989).
- [4] B. C. Giessen and C. Borromee-Gautier, J. Sol. State Chem. 4, 447 (1972)
- [5] J. M. del Pozo and L. Díaz, (To be published).



**AN IMPROVED METHOD FOR THE CALCULUS OF ACTIVATION ENERGY
SPECTRA (AES) IN THE ANALYSIS OF RELAXATION EXPERIMENTS.**

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Analysis of relaxation experiments has often employed the theoretical AES model introduced by Primak and Gibbs. In this method, the change during relaxation at temperature T of a measured property, ΔP , is expressed by means of a Volterra integral equation of the first kind

$$\Delta P(t) = \int_0^t p_0(E) \theta(E, T, t) dE$$

with kernel the characteristic θ -function, and where $p_0(E)$ is the total property change in the energy range E to E + dE. By performing a step-like approximation for $\theta(E, T, t)$ we find the simple Primak's energy derivative method. This procedure of obtaining the $p_0(E)$ spectrum works well if the experiment involves a very broad and smooth AES. Unfortunately, it is no longer possible in practice to support this assumption and there is a need to develop a better and more general procedure.

In the present work, a deeper insight into this problem is afforded by considering the true $\theta(E, T, t)$ functional form and by replacing the integral equation by a set of linear equations. Insofar we are faced with a so-called "ill-conditioned" system, resort to the variational Cook's "least structure analysis" allow us to get stable and smooth solutions. The method is of such a kind that it approaches, as closely as desired, the true solution.

In order to asses the performance, we compare the Primak's approximate method versus the improved one for two cases:

- mechanical stress relaxation experiments on CoO single crystals in the range 77K-289K.
- enthalpic relaxation in amorphous Se around T_G .

The success of this procedure proved quite spectacular.

**NEUTRON SCATTERING FROM AMORPHOUS
HYDROGENATED CARBON**

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An extensive study of amorphous hydrogenated carbon, a-C:H (often referred to as diamond-like carbon by virtue of its unique mechanical and optical attributes) has been conducted using the facilities at the ISIS pulsed neutron source. Diffraction data is now available out to Q-values of 50 \AA^{-1} . This wide range ensures a real-space resolution sufficient to resolve directly the contributions from the principal C-C bond types and to provide evidence for the existence of molecular hydrogen.

In addition, inelastic incoherent neutron scattering has been used in an attempt to study in more detail the nature of the hydrogen environment. In particular, a simple force-field model has been used to model the vibrational density of states and thereby to identify the principal structural units associated with bonded hydrogen. These experiments have also provided further evidence for the presence of molecular hydrogen.

A.C. CONDUCTIVITY OF AN AMORPHOUS NIOBIUM PHOSPHATE

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An amorphous potassium niobium phosphate $K_{0.5}NbOPO_4 \cdot 2.2H_2O$ with a BET surface area of 234 m²/g and a pore size of 42 Å Ø has been synthesized. For the synthesis of this amorphous solid, the method described by Hahn (J. Am. Chem. Soc. 73, 5091-5093, 1951) with a modification from us was used. (Cantero-Sanchez F. et al, Inorg. Chem. submitted 1991). Its spectroscopy properties indicates a low concentration of isolate OH⁻ group (P-OH and Nb-OH), being more important the systems hydrogen-bonds and/or by water molecules.

A.C. conductivity measurements between 313 K and 473 K were performed using a Solartron 1255 Frequency Response Analyzer controlled by computer. The experimental results were fitted to the universal response ($\sigma(\omega) = \sigma_0 + A\omega^n$) where σ_0 is the d.c. conductivity, A is a temperature dependent parameter and n is found to take values between 0 and 1. The universal response provides a simple method to obtain the hopping rate of ion (ω_p). For temperatures below 373K the compound shows a low activation energy and the ion mobile concentration is thermally activated. For temperatures higher than 373K the amorphous shows a higher activation energy and the ion mobile concentration is independent of the temperature.

| | | | | | | | | | | |
|---|------|------|------|-----|-----|-----|------|------|------|------|
| T (K) | 313 | 333 | 363 | 383 | 393 | 423 | 433 | 443 | 453 | 473 |
| σ (S cm ⁻¹).10 ⁻⁸ | 74 | 105 | 124 | 2.9 | 4.8 | 9.8 | 12.7 | 16.3 | 20.8 | 33.6 |
| ω_p (sec ⁻¹) | 2384 | 2539 | 2716 | 60 | 107 | 234 | 433 | 409 | 545 | 955 |

DIELECTRIC RELAXATION IN GLASSES WITH COMPOSITION



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The physical mechanisms that contribute to polarisation in a material may be studied from the analysis of depolarisation current. Our previous results on the glasses had suggested that the information about the relaxation parameters can be used to distinguish different types of relaxing ions in an amorphous structure. In this line of action we have measured the depolarisation current in lead borate glasses with different concentrations of Eu_2O_3 , over a wide range of temperature. Each specimen was subjected to an electric field of 100 KVm^{-1} and then the current was measured every second. The experimental results were fitted to the stretched exponential function $\phi = \phi_0 \exp[-(t/\tau)^\beta]$ with the subsequent determination of the relaxation parameters ϕ_0 , τ and β . We observe a weak dependence of parameters with concentration, but a relatively strong dependence on the temperature.

OPTICAL PROPERTIES AND ENERGY TRANSFER
AMONG 4f IONS IN FLUORZINCATE GLASSES

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Optical absorption and emission spectra have been studied for Sm^{3+} and Tb^{3+} ions in $\text{ZnF}_2\text{-CdF}_2$ based glasses with concentrations in the range 0.1-2.5 mol%.

The measured oscillator strengths and radiative rates for several transitions are compared with values calculated using the Judd-Ofelt theory. the agreement is fairly good.

The radiative lifetime of the fluorescent $^4\text{G}_{5/2}$ level of Sm^{3+} has a value of 5.25 ms. In glasses with Tb^{3+} emission is observed from the $^5\text{D}_3$ and $^5\text{D}_4$ levels; the first presents thermalization effect and the obtained effective lifetimes are 2 and 4.9 ms respectively.

The interaction between adjacent ions has been investigated. The decay curves become nonexponential when the Sm^{3+} or Tb^{3+} concentration is larger than 0.1 mol%. It can be explained by cross relaxation.

The mechanism of interaction among Sm^{3+} or Tb^{3+} ions has dipole dipole character and the parameter of transfer C_{DA} for cross relaxation is two orders of magnitude larger than the parameter C_{DD} for energy migration.

**STRUCTURAL MODIFICATIONS IN XEROGELS PREPARED USING
SONOCATALYSIS AND AN ADDITIVE**

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The fabrication of monolithic glasses by sol-gel method is widely studied because of their optical properties. The obtention of gels is possible by the hydrolisis of a metallic alkoxide and polycondensation of silicic acid. The ultrasound energy applied to the hydrolisis reaction allows the obtention of gels without the use of any solvent. The structure of resulting xerogels is modified by the ultrasound and its dose. The addition of a chemical additive during the hydrolisis reaction has an important role during the drying because of its control in the solvents leaving the wet gel. But the additive also seems to have an important effect in the xerogel structure. Therefore, the study of how these modifiers, additive and ultrasound, change xerogel structure and its evolution with the heat treatment is important when the obtention of monolithic glasses is required. Experimental results from Small Angle X-ray Scattering (SAXS) and Nitrogen Adsorption-Desorption isotherms permit to propose a model to explain structure evolution during the densification into glass.

ON THE SINTERING OF MIXED AEROGELS

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Mixed $\text{TiO}_2\text{-SiO}_2$ sonogels and classic gels were dried on hypercritical conditions and submitted to a halogen treatment for dehydroxilation. The resulting porous aerogels were partially densified at several temperatures. In this work we use Small Angle X-Ray Scattering (SAXS) technique to study the evolution of the ultrastructure on sintering both kind of aerogels. The analysis of the scattering intensity profile indicates that the texture of these gels leads to deviations of the limiting slopes from the Porod's law which differs depending on the nature of the initial gel.

**TEXTURAL FEATURES OF SILICA-TITANIA AEROGELS
PREPARED BY THE SONOCATALYTIC METHOD**

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A series of $\text{TiO}_2\text{-SiO}_2$ gels with different $[\text{Ti}]/[\text{Si}]$ ratio was elaborated by the sonogels method using acetic acid as chelating agent for the titanium precursor. Supercritical drying of these gels was accomplished leading to highly porous aerogels which were compared with the classic counterpart of the same composition.

In this paper, microstructural features of both kinds of aerogels are investigated on several levels in the light of the results obtained from the analysis of the N_2 -adsorption/desorption and Small Angle X-Ray Scattering (SAXS) data and transmission electron microscopy (TEM).

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